# APPLIED Spectroscopy

1961
Vol. 15 No. 3

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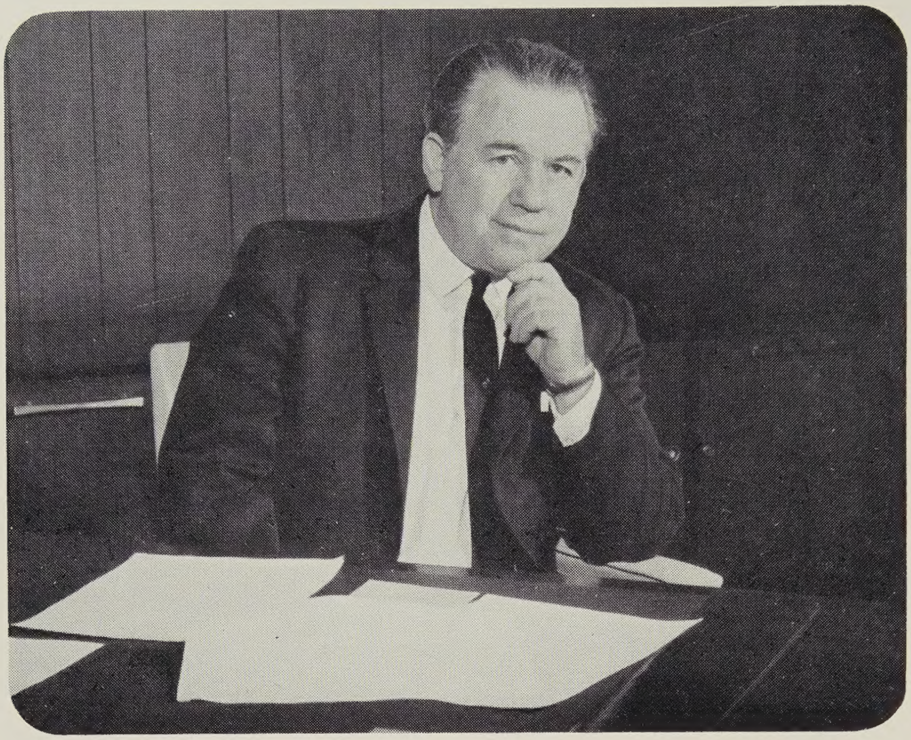

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APPLIED SPECTROSCOPY

Vol. 15, No. 3 1961

## Table of Contents

PAPERS

The Analysis of Unirradiated "Fissium" Alloy by Optical Emission Spectroscopy—*Joseph A. Goleb* ..... 57

Identification of Barbiturates by X-Ray Diffraction Powder Patterns of Their p-Nitrobenzyl Derivatives—*J. A. R. Cloutier and Jane M. Manson* ..... 60

Mass Spectrometry of Some High Molecular Weight Aliphatic Acids and Their Methyl Esters.
Analysis of Nonanoic and 2-Ethylheptanoic Acid Mixtures—*Fred M. Trent and Franklyn D. Miller* ..... 64

Pressure-Broadening Effects on Infrared Peak Intensities of Hydrocarbons—*A. P. Altshuller and A. F. Wartburg* ..... 67

The Spectrochemical Analysis of Magnesium and Its Alloys for Beryllium, Lead and Other Trace Elements by Solution and Salt-Cap Techniques—*R. E. Mansell* ..... 70

Soviet Spectrographic Equipment—*M. Malinek* ..... 73

Physico-Chemical Characterization of Some 5,5-Disubstituted 1:3-Dimethyl Barbituric Acids—*Jane M. Manson and J. A. R. Cloutier* ..... 77

NOTES

A Simple Method of Improving Sensitivity in the Infrared Determination of Sulfate—*J. W. Nehls and J. A. Wheat* ..... 80

SPECTROGRAPHIC TRICKS

Long Path Infrared Microcell—*D. S. Erley* ..... 80

Heated Cell for Thermal Stability Studies of Polymers Using Infrared Spectroscopy—*Robert T. Conley and Joseph F. Bieron* 81

Modifications to Spectrum Plate Comparator to View Overlapping Wavelength Ranges—*H. P. Rothbaum and H. J. Todd* ..... 82

Supplementary Optics for Perkin-Elmer Model 21, Double Beam Infrared Spectrophotometer—*L. H. Little* ..... 83

INFRARED QUANTITATIVE ANALYTICAL DATA ..... 84

COLUMNS AND FEATURES

What's New? 7A, The Spectral Line 9A, Book Review, "X-Ray Absorption and Emission in Analytical Chemistry",—Liebhafsky, Pfeiffer, Winslow and Zemany 86, S.A.S. Local News 87, News of Other Societies and Institutions 88, Publications Accepted 17A, Bibliography 17A.

## Index to Advertisers

APPLIED PHYSICS CORP. ..... 9A
*Agency*—Clyde D. Graham, Los Angeles, Calif.
APPLIED RESEARCH LABORATORIES ..... 13A
*Agency*—Willard G. Gregory & Co., Los Angeles, Calif.
BAIRD-ATOMIC, INC. ..... Inside front cover, 11A
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BECKMAN INSTRUMENTS, INC. ..... 6A
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*Agency*—Central Adv. Service, Chicago, Ill.
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*Agency*—George T. Metcalf Co., Providence, R. I.
ISOMET CORP. ..... 87
*Agency*—Larry Alpaugh, Westwood, N. J.
JARRELL-ASH CO. ..... Outside back cover
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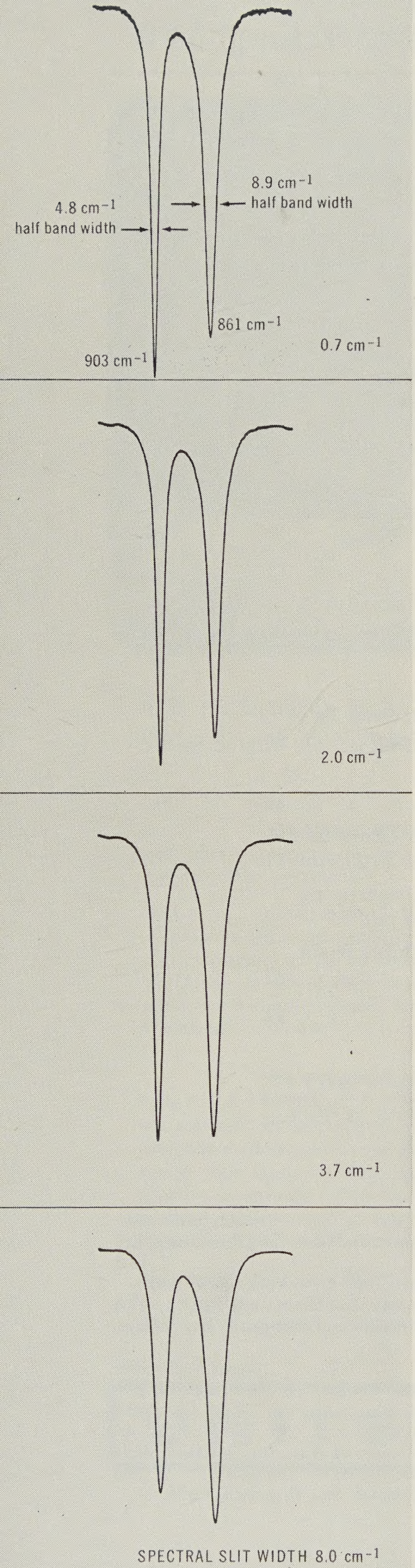

*Left, spectrum of a 0.21 mm. thickness sample of spectro-grade cyclohexane demonstrates the importance of high resolution for* routine *quantitative analysis.*

*Right, the C-H stretching band of methane illustrates the increased* research *data obtainable with high resolution spectroscopy.*

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High resolution of the Beckman IR-7 does more than merely separate closely spaced neighboring bands. Note, for instance, how the apparent intensities of the two cyclohexane bands increase with higher resolution. The relatively greater increase in the intensity of the 903 cm$^{-1}$ band at higher resolutions is the result of its narrower half-band width. These two commonly analyzed samples demonstrate the importance of high resolution in both low and high frequency regions and, for both gas and liquid samples. Comparative spectra were run with identical samples; slit width and resolutions, were varied as noted. ⌘ High resolution is essential for *all areas of spectroscopy;* for studies of molecular motion and structure, for differentiating between substances which exhibit similar spectra, and also for providing increased sensitivity and absolute accuracy for quantitative analysis. A further long-run advantage of high resolution is the increased potential for transferring data from one instrument to another. For more information about high resolution spectrophotometers, including indene spectra, write for Data File 39-4-02.

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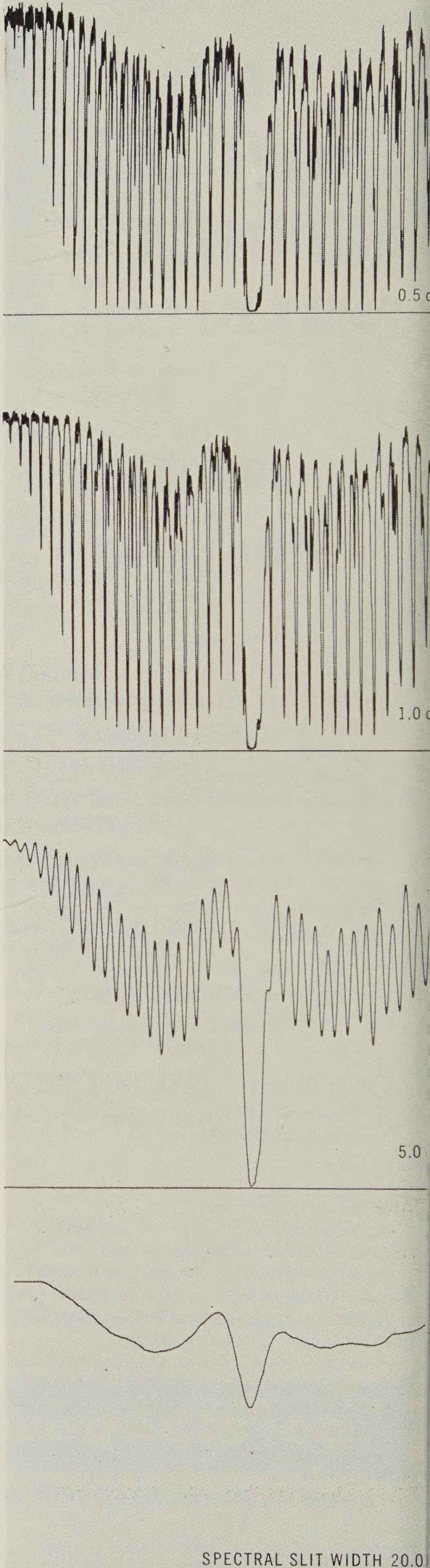


# What's New?

## Editor—Rodger W. Loofbourow

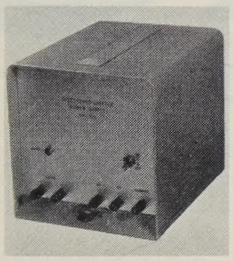
**[Contributions for this column should be sent to the Editor, Rodger W. Loofbourow, Crobaugh Laboratories, 3800 Perkins Avenue, Cleve'and 14, Ohio.]**

Following the announcement, carried in our previous issue, of the formation of Scope, Inc., we have been informed that the office and plant of the organization is located at 10 Jefferson Avenue, Woburn, Massachusetts and that the founding officers are, Jason Saunderson, President; Eliot DuBois, Engineering; Paul Hutchinson, Treasurer; Henry Levesque, Sales; and Williard Ferguson, Controller. Scope, Inc., plans to offer *consultive services* in addition to the *development, manufacture,* and *sale of analytical instruments.*

λ

Labgear Limited, Cambridge, England offers a new *Spectrophotometer Power Supply.*

Designated the Type 115D, this unit can be powered from either a 110V or 220V line and delivers either 2V or 6V output with a stability factor greater than 1000:1.



λ

An *Atomic Absorption Apparatus,* the AT-6, is available from Optica, Inc., Washington, D.C.

This instrument features a six-place lamp turret, a double beam optical system, a prism monochromator, and a multiple orifice burner. Hollow cathode lamps for twenty elements are available and more are in preparation.

λ

Jarrel-Ash Company, Newtonville, Massachusetts has announced three developments in their line of instruments and services.

1—They are the exclusive representatives of the *Polarlog* in the United States. This instrument is a polarograph, which can operate on AC, producing results in the form of peaks rather than the conventional step type polarogram. This feature provides a substantially improved resolution of decomposition potentials and permits determination of concentration by measuring peak heights. The instrument can also be operated on a conventional dc current.

2—Their *grating* production facilities have been expanded, and they are now able to produce replica gratings up to 3″ x 7″. They are also exclusive representatives in this country of Paton-Hawksley Company of England and supply their complete line of gratings designed for infrared, meterology and education. A catalog listing the complete line of gratings is available.

3—*Laboratory services* have been extended to include gas chromatography, X-ray diffraction, dissolved oxygen and fluorometry.

λ

Two new accessories for the *Cary Spectrophotometer* have been announced by Applied Physics Corporation, Monrovia, California.

1—The *Repetitive Scan Accessory* permits the unattended operation of the spectrometer over a preselected wave length span. The scan can be repeated automatically at predetermined time intervals with the spectra appearing in sequence on the chart paper.

2—The Model 2015 *Absorptivity Recorder* is used with the spectrophotometer to record absorptivity (extinction coefficient) on a logarithmic scale. This accessory provides spectra whose shape is unaffected by sample concentration or path length.

λ

The new Cahn *Recorder Control,* available from Cahn Instrument Company, Paramount, California, converts any fixed-span recorder to a universal multirange recorder with 15 voltage ranges and 15 current ranges. This control can be used directly with all types of potentiometric recorders and d'Arsonval recorders with vacuum tube preamplifiers.

λ

A new *ESR Spectrometer* has been announced by the Ridgefield Instrument Group, Ridgefield, Connecticut.

It is claimed that this instrument can be operated on routine analyses by a laboratory technician and that the sensitivity is such that precise quantitative electron spin resonance measurements can be made on wet chemical and biomedical samples. The instrument is based on the design of Dr. Jonathan Townsend of Washingington University.

λ

Arthur H. Thomas Company, Philadelphia, Pennsylvania has announced the publication of a new Scientific Apparatus and Reagents *Catalogue.*

λ

A technical brochure on the newly-announced A-60 *Analytical NMR Spectrometer* System has been published by the Instrument Division, Varian Associate, 611 Hansen Way, Palo Alto, Calif. The 16-page brochure, illustrated with photographs and technical diagrams, includes discussions of range of applications, ease of operation and maintenance, theory of A-60 operation with special emphasis on the unique Varian NMR Field/Frequency Control System, and performance specifications. This unique instrument was first shown to the public in February at the 12th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. It is a compact, simplified yet sophisticated version of Varian's famed HR-60 High Resolution NMR Spectrometers.

λ

The Optical Society of America has been translating Optika i Spektroskopiya and distributing this monthly journal free to all OSA members and subscribers to the Journal of the Optical Society of America. This free distribution was an experiment for three years, so that the individual reader might become accustomed to reading a translation journal not as an oddity but as a publication that is looked for each month. In December of this year the National Science Foundation grant, which helped to publish the journal, ends, but the interest in Optics and Spectroscopy is now too lively to be discontinued, so the *OiS CLUB SCHEME* has been evolved. This is a special subscription rate for members of those societies who wish to take part in the OiS CLUB SCHEME, viz:

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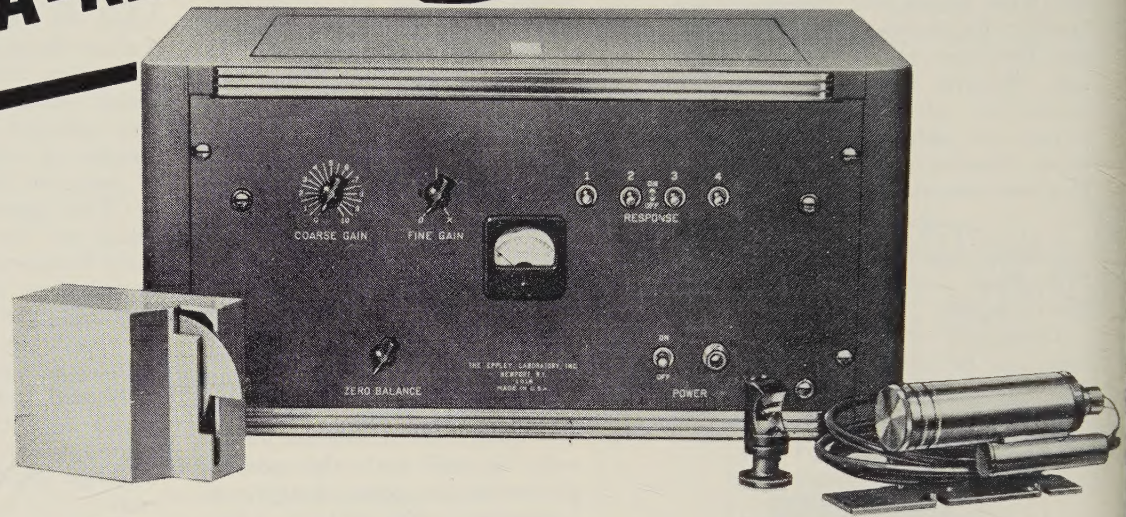
If a translation journal is to be of real use, it should be read widely by all the people working in the field, and these research results should be made available in the shortest possible time. Optics and Spectroscopy is published in English translation within three months of the Russian edition coming out e.g. the March 1961 issue will be published in English on June

*(Continued on page 13A)*

# A Superior Detector for INFRA-RED SPECTROSCOPY



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*Fundamental and experimental aspects of this detector are discussed in the following publications: Rev. Sci. Inst. **18**, 347 and 357 ('47); ibid. **20**, 816 ('49); Proc. IRE **40**, 1161 ('52).

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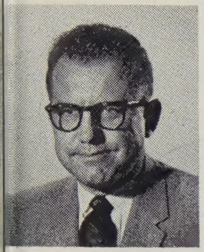
# The Spectral Line

## Editor—S. Richard Wiley

**[News about members and matters of interest to spectroscopists may be sent to the Editor, S. R. Wiley, 1239 Owen Brown Rd., Ellicott City, Md.]**



*Donald R. Moore,* 45, Vice President for Sales, National Spectrographic Laboratories, died April 10th, in Cleveland, Ohio. Mr. Moore had been on the NSL staff since 1950. Prior to joining NSL, he was research supervisor for Babcock & Wilcox Company. A graduate of Mount Union College (1938) with a BS degree in Chemistry, Mr. Moore also attended graduate school at Ohio State University. He was a member of the American Society for Metals, Society for Applied Spectroscopy, and the Chemists Club of New York.

*Dr. Glenn H. McIntyre,* President of NSL, will temporarily assume the additional sales duties of Mr. Moore.

——— λ ———

*Allen H. Okamoto* is now associated with the technical staff of the General Electric Co., Missile and Space Vehicle Department, 3750 "D" Street, Philadelphia 24, Pa. Allen is Assistant Business Manager of Applied Spectroscopy. He was formerly a spectroscopist at the Research and Development Division of the Atlantic Refining Company.

——— λ ———

*Ed Van Dien* is now managing a commercial spectrographic laboratory in northern New Jersey, offering emission analysis and consulting services. He was formerly the representative in that area for Applied Research Laboratories.

——— λ ———

*William E. Allsopp* is now Sales Manager of the Industrial Division of Williams Gold Refining Company, Buffalo, N. Y. He was associated formerly with the United Carbon Company.

——— λ ———

*Rolf Lindenhayn, Jr.* has been appointed a western division manager for National Carbon Company. Among his responsibilities is the marketing of spectroscopic electrodes and powders.

——— λ ———

*Claire Bell* has joined Varian Associates as manager, instrument product engineering. Mr. Bell will be responsible for product engineering for the division's entire line of spectrometers,

*(Continued on page 17A)*

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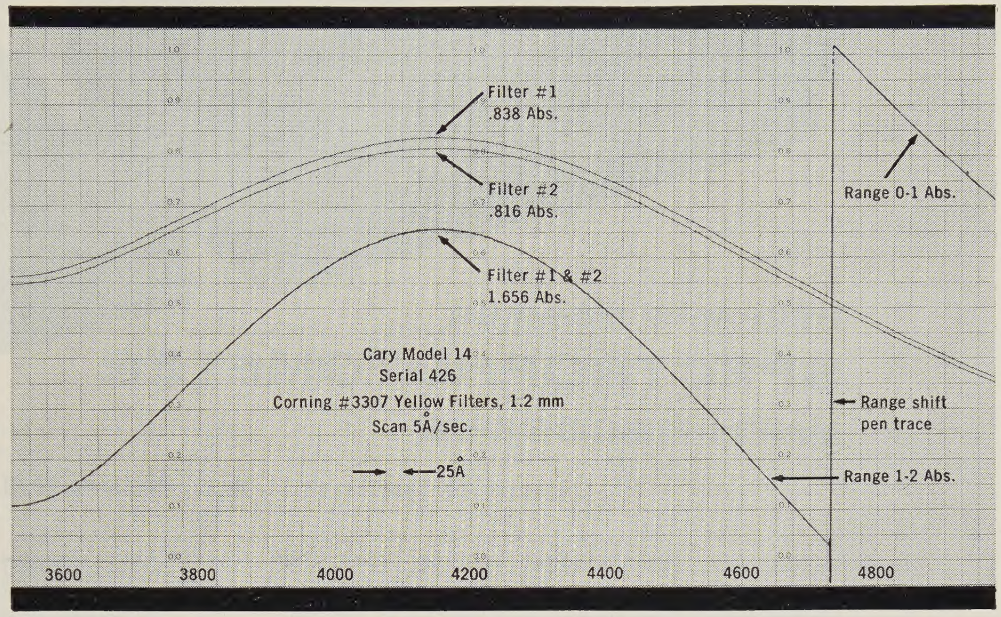
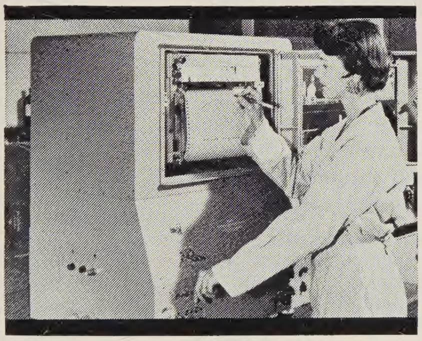


Cary Model 14 records spectra accurate and reproducible to .002 at 1.0 absorbance unit, to .005 at 2.0



High photometric accuracy and reproducibility are essential to provide reliable data for correctly interpreting scientific studies. These features also are of prime importance in control analyses where product quality or important production decisions are based on analytical results.

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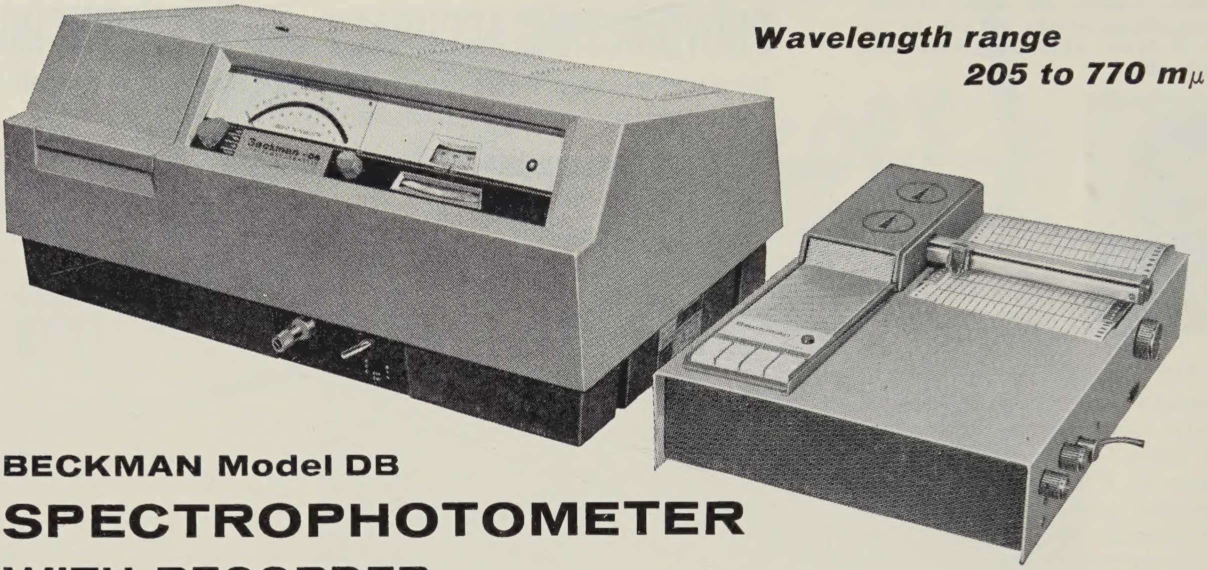

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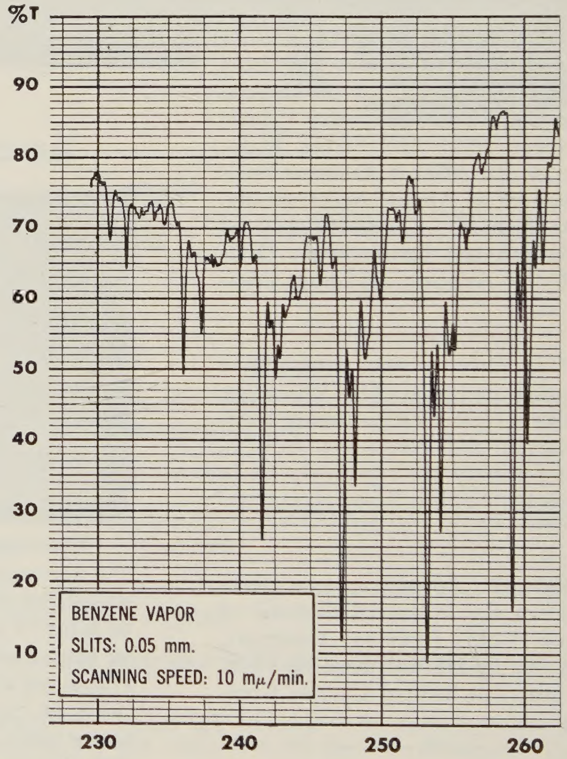

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APPLIED SPECTROSCOPY

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# The Analysis of Unirradiated "Fissium" Alloy by Optical Emission Spectroscopy†

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## Abstract

An optical emission spectrographic method has been developed for the quantitative determination of molybdenum, ruthenium, rhodium, palladium, and zirconium in normal uranium metal in the range of 2.5%, 2.0%, 0.30%, 0.20%, and 2.5%, respectively. The precision of the spectrographic method for molybdenum is ±1.0%, ruthenium ±1.8%, rhodium ±1.7%, palladium ±2.1%, and zirconium ±2.2% of the amounts present. The comparison of spectrographic and chemical results on 24 "fissium" alloy samples for molybdenum, ruthenium, rhodium, palladium, and zirconium shows a standard relative deviation from the chemical results of ±3.9%, ±4.3%, ±7.2%, ±6.6% and ±7.5%, respectively. These samples were chosen at random from ingots by using routine sampling procedures.

## Introduction

In the building of nuclear reactors at the Argonne National Laboratory, numerous analytical problems arise concerning fuel and construction material that require special techniques and equipment. The spectrographic laboratory of the Argonne National Laboratory is very often called upon to help with these analytical problems.

In the past, graphite *(1)*, lithium-aluminum alloys *(2)*, and the metals zirconium *(3, 4)*, thorium *(5, 6)*, plutonium *(7)*, and beryllium *(8)* have been analyzed for minor impurities by spectrographic techniques developed at this laboratory. Also in the construction of the Experimental Boiling Water Reactor, the spectrographic laboratory developed a method for the quantitative determination of zirconium and niobium in the ternary uranium fuel material *(9)*.

Recently, unirradiated normal uranium alloys, commonly called "fissium" alloys, containing approximately 2.5% molybdenum, 2.0% ruthenium, 0.20% rhodium, 0.30% palladium, and 2.5% zirconium have been synthesized at the Argonne National Laboratory to simulate the highly irradiated melt refined "fissium" alloys. Since it appears that synthesized "fissium" alloys and highly irradiated melt refined "fissium" alloys have similar chemical and metallurgical properties *(10)*, much experimental work was carried on with the former, because they were easier to handle.

This paper describes a spectrographic method for the determination of molybdenum, rhodium, ruthenium, palladium, and zirconium in normal uranium metal using essentially the same technique mentioned previously *(9)*.

## Outline of Method

The spectrum of the "fissium" alloy is extremely complex *(11, 12)*, and many of the spectral lines have a high non-uniform accompanying background *(13)*. In order to obtain the sensitivity and accuracy in the determination of the alloying constituents in "fissium" alloy, the freshly machined surface of the alloy was sampled directly by the high voltage condensed ac spark *(14)*. It was decided to use this type of source, since it provided excitation of considerably greater flexibility and reproducibility than either the ac or dc arc. The point-to-plane technique *(15)* was used with the Petrey stand to accommodate samples of irregular sizes and shapes that ranged in weight from 5 g to 1 Kg. Plates were calibrated using an emulsion calibration curve obtained with a dc arc and rotating step sector *(16)*. The intensity ratios of analytical lines and uranium lines were determined photometrically.

## Standards

The preparation of valid standards for spectrographic analysis is an important and critical phase of research. Four standard "fissium" alloys were compounded, ranging in composition from approximately 15 wt % "fissium" to 3.8 wt % "fissium." In these alloys the aggregate of the elemental species molybdenum, ruthenium, rhodium, palladium, and zirconium contained is termed "fissium" with the balance of the composition being uranium.

The technique employed in producing this series of "fissium" alloys involved the compounding of the highest "fissium" composition first and obtaining the lower "fissium" compositions by successive dilutions with unalloyed uranium. The 15% "fissium" alloy was compounded by induction melting in a vacuum of the order of 5 x $10^{-5}$ mm Hg. High purity magnesia was used for the crucible and stopper rod, but the molten alloy was cast in a thoria coated graphite mold. The melt was held at 1450°C for ½—¾ hrs before being bottom poured at 1400°C. This alloy then served as the starting material for the compounding of all of the succeeding lower "fissium" alloys.

The uranium in these alloys was commercially produced metal. High purity magnesia ceramics and a thoria coated graphite mold were also used in this premelting operation. The working vacuum was of the order of 2 x $10^{-4}$ mm Hg and the casting temperature in the range 1450—1500°C.

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†Based on work performed under the auspices of the U. S. Atomic Energy Commission.

The zirconium additions were made in the form of ¼ in. diam. by ¼ in. long pieces obtained from ⅝ in. diam., grade-III crystal bar by swaging. The molybdenum was in the form of ¼ in. x ¼ in. scraps of ⅛ in. thick plate. All remaining alloying elements were obtained commercially in powder form, and subsequently compressed into ¼-in. diam. compacts and arc melted to produce solid buttons.

The actual standard specimens of each composition were injection cast as 0.144-in. diam., 14¼-in. long rods. Precision bore, Vycor glass tubes whose inside surface had been coated with thoria were used as molds. In this casting process the "fissium" alloys were induction melted in thoria coated graphite crucibles in a vacuum of the order of 6 x $10^{-5}$ mm Hg. The 5 Wt % "fissium" alloy was injection cast into pin specimens by a simple remelting operation. Each of the subsequent "fissium" compositions were compounded and injection cast in a single operation by using the proper ratio of fissium master alloy and unalloyed uranium. Casting temperatures varied arbitrarily between 1290 and 1400°C. The rapid cooling of the cast rods within the Vycor molds results in minimum segregation.

See Table I for chemical analysis of spectrographic standards.

TABLE I. CHEMICAL ANALYSIS OF SPECTROGRAPHIC STANDARDS

| *Standard No.* | *Molybdenum %* | *Ruthenium %* | *Rhodium %* | *Palladium %* | *Zirconium %* |
|---|---|---|---|---|---|
| SF-1 | 5.06 | 4.14 | 0.534 | 0.390 | 5.78 |
| SF-2 | 2.58 | 2.18 | 0.282 | 0.206 | 3.03 |
| SF-3 | 3.44 | 2.86 | 0.364 | 0.278 | 4.08 |
| SF-4 | 1.04 | 0.865 | 0.0938 | 0.0821 | 1.14 |

## Procedure

A sample was machined until a clean, smooth, flat surface having an area of approximately ⅛ in. diam. or greater, was available. The sample served as the upper electrode of the Petrey stand, and a minimum of 5g was used to prevent overheating. A pointed ⅛ in. diam. graphite electrode having one end machined to a 15° cone was used as the counter electrode. The electrode spacing was 4 mm.

The sample was presparked for 5 sec and exposed for 18 sec. The exposure index of the 2660.14 uranium line was approximately 15% transmittance. A modified Baird spark source was used with a 5 mm air-interrupted gap, and additional capacitance was employed with the following electrical parameters:

| | |
|---|---|
| Primary | 130 v, 5.5 amp |
| Secondary | 25,000 v |
| Inductance | 4.06 μh |
| Capacitance | 0.005 μfd |
| Resistance | Residual |
| Radio-frequency current | 6.5 amp |
| Discharge per cycle | 2 |

These excitation conditions were selected because the spark discharge produced did not appreciably burn or oxidize the alloy. Hence reproducible photographic exposures of the spectrum were obtained. The excitation index or intensity ratio of the U I-2935.15/U II-3025.03 was 1.38, using exposure conditions outlined above and a uranium alloy of nominal composition.

TABLE II. ANALYTICAL AND URANIUM INTERNAL STANDARD LINES USED FOR ALLOY ANALYSIS

| *Wavelengths of Analytical Lines, A* | *Wavelengths of Uranium Lines, A* | *Concentration range, %* | *Concentration index, %* |
|---|---|---|---|
| Molybdenum - 2660.58 | 2660.14 | 1.0 -5.0 | 2.3 |
| Ruthenium - 2661.61 | 2660.14 | 1.0 -4.0 | 2.0 |
| Rhodium - 2461.04 | 2460.86 | 0.10-0.50 | 0.25 |
| Palladium - 2488.92 | 2492.95 ± .03[a] | 0.10-0.40 | 0.13 |
| Zirconium - 2449.85 | 2397.32 | 1.0 -6.0 | 2.4 |

[a] Unlisted line

A large Littrow quartz spectrograph having a dispersion of 1.93 A/mm at 2333 A was employed. This instrument has sufficient dispersion and resolving power at the low wavelength region to minimize the mutual interferences between the lines of uranium and the alloying constituents. A 16 cm quartz lens was used to form the image of the electrodes on the collimator of the spectrograph. An aluminized quartz plate giving a transmittance of approximately 20% was used next to the slit of the spectrograph to reduce the spectral intensity.

The spectrum was recorded on an Eastman Spectrum Analysis No. 1 plate that was processed using standard darkroom techniques. The relative transmittance of the spectral lines and their adjacent backgrounds were measured with a Jarrell-Ash microphotometer. The relative transmittance of the analytical lines, internal standard lines, and adjacent background, were converted to log relative intensities. Intensity ratios were obtained after subtracting background *(17)* using a Respectra calculating board with an appropriate emulsion calibration curve. Log intensity ratios were converted to concentration by reference to an analytical curve previously determined. This was a plot of log intensity ratio against log concentration obtained from chemically analyzed standards.

## Results

Table II shows the analytical and internal standard lines used. These lines were selected because of optimum intensities for the specified composition, freedom from interferences due to alloying elements or residual impurities, and uniformity of background for each line pair. Several uranium internal standard lines instead of one were used to provide background and line intensities nearly equal to the analytical line intensity for the nominal composition, thereby reducing errors due to change in plate calibration and sensitivity. Optimum intensites for the spectral lines used were obtained by a single exposure.

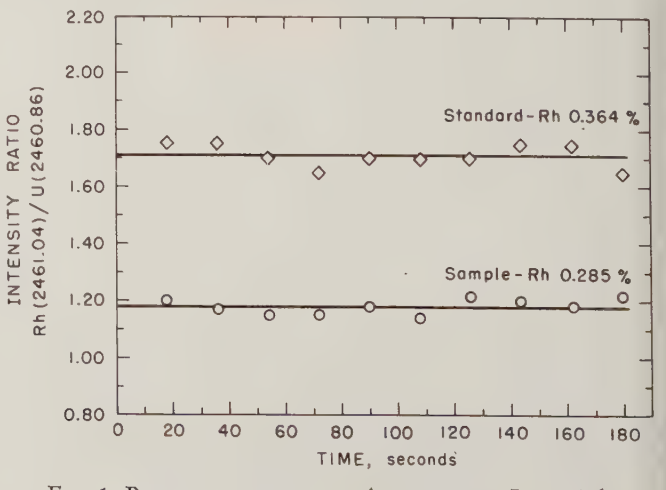

FIG. 1. REPRODUCIBILITY OF ANALYTICAL LINE, Rh 2461.04 A, AND INTERNAL STANDARD LINE, U 2460.86 A

Table III. Comparison of Spectrographic and Chemical Determinations of Molybdenum and Ruthenium in "Fissium" Alloy

| Sample No. | % MOLYBDENUM Spec. | Chem. | Rel. Dev., % | % RUTHENIUM Spec. | Chem. | Rel. Dev., % |
|---|---|---|---|---|---|---|
| 1 | 2.63 | 2.44 | 7.8 | 2.03 | 2.06 | 1.5 |
| 2 | 2.53 | 2.49 | 1.6 | 2.01 | 2.02 | 0.5 |
| 3 | 2.68 | 2.59 | 3.5 | 2.19 | 2.10 | 4.3 |
| 4 | 2.53 | 2.54 | 0.4 | 2.10 | 2.08 | 1.0 |
| 5 | 2.48 | 2.48 | 0.0 | 2.00 | 2.05 | 2.4 |
| 6 | 2.47 | 2.48 | 0.4 | 2.03 | 2.00 | 1.5 |
| 7 | 2.48 | 2.41 | 2.9 | 2.03 | 1.99 | 2.0 |
| 8 | 2.42 | 2.48 | 2.4 | 2.00 | 2.13 | 6.1 |
| 9 | 2.52 | 2.48 | 1.6 | 2.07 | 2.04 | 1.5 |
| 10 | 2.50 | 2.51 | 0.4 | 2.08 | 2.08 | 0.0 |
| 11 | 4.95 | 5.15 | 3.9 | 4.25 | 4.26 | 0.2 |
| 12 | 5.05 | 5.10 | 1.0 | 4.22 | 4.22 | 0.0 |
| 13 | 2.72 | 2.44 | 11.0 | 1.05 | 1.12 | 6.3 |
| 14 | 2.58 | 2.48 | 4.0 | 0.99 | 1.12 | 12.0 |
| 15 | 2.31 | 2.48 | 6.8 | 1.80 | 1.98 | 9.1 |
| 16 | 2.50 | 2.44 | 2.5 | 1.90 | 2.04 | 6.9 |
| 17 | 1.68 | 1.64 | 2.4 | 1.34 | 1.30 | 3.1 |
| 18 | 1.72 | 1.64 | 4.9 | 1.23 | 1.26 | 2.4 |
| 19 | 1.69 | 1.64 | 3.0 | 1.32 | 1.28 | 3.1 |
| 20 | 1.68 | 1.66 | 1.2 | 1.33 | 1.32 | 0.8 |
| 21 | 2.46 | 2.44 | 0.8 | 2.04 | 1.99 | 2.5 |
| 22 | 2.47 | 2.47 | 0.0 | 2.04 | 2.02 | 1.0 |
| 23 | 3.31 | 3.26 | 1.5 | 2.70 | 2.72 | 0.7 |
| 24 | 3.40 | 3.34 | 1.8 | 2.75 | 2.76 | 0.4 |
| Std. Rel. Dev., % | | | ± 3.9 | | | ± 4.3 |

To test the reproducibility of the analytical lines and internal standard lines a homogeneous sample and standard were sparked continuously for 180 sec to obtain 10 separate exposures. Ratios of the line pairs were calculated and plotted against exposure time. Figure 1 is typical of line pairs used. The straight lines in Figure 1 that are parallel to the abscissa indicate the line pairs had proper excitation characteristics, and no differential heating effect or volatilization occurred on the part of the sample or standard.

No analytical curves are illustrated. They are straight lines drawn through a small dispersion of points indicating good spectrographic and chemical reproducibility, stable analytical lines, and proper background corrections.

Tables III, IV, and V show the comparison of chemical and spectrographic results. All spectrographic results are the average of 4 separate exposures taken from one continuous 92 sec sparking.

In a metallurgical program involving the casting of samples of different geometrical shapes and sizes the problem of segregation is of much concern to the analyst as well as the metallurgist. It was thought that this spectrographic method lends itself readily to the homogeneity study of the alloying elements in uranium, since the point-to-plane technique utilized a very small amount of sample. Protrusions from castings were checked for heterogeneity at ⅛ in. intervals. Also, pins approximately ⅛ in. diam. and 14 in. long were analyzed at 3-in. intervals for segregation. Results from these tests proved valuable to a reactor program that was seeking a homogeneous "fissium" fuel alloy.

## Discussion

In developing this spectrographic method the advantages, if any, in speed and accuracy had to be determined, and accountability of special materials considered.

In a research and developmental reactor program an early knowledge of the composition of the fuel material is important, since subsequent work depends upon the analysis. Using this spectrographic procedure, 10 samples were analyzed in quadruplicate in an 8-hr day for 5 elements by one analyst.

Table IV. Comparison of Spectrographic and Chemical Determinations of Rhodium and Palladium in "Fissium" Alloy

| Sample No. | % RHODIUM Spec. | Chem. | Rel. Dev., % | % PALLADIUM Spec. | Chem. | Rel. Dev., % |
|---|---|---|---|---|---|---|
| 1 | 0.300 | 0.290 | 3.5 | 0.193 | 0.206 | 6.3 |
| 2 | 0.287 | 0.273 | 5.1 | 0.193 | 0.203 | 5.0 |
| 3 | 0.295 | 0.298 | 1.0 | 0.202 | 0.218 | 7.3 |
| 4 | 0.295 | 0.296 | 0.3 | 0.199 | 0.215 | 7.4 |
| 5 | 0.285 | 0.296 | 3.7 | 0.192 | 0.206 | 6.8 |
| 6 | 0.291 | 0.285 | 2.1 | 0.203 | 0.204 | 0.5 |
| 7 | 0.291 | 0.260 | 12.0 | 0.192 | 0.198 | 3.0 |
| 8 | 0.288 | 0.271 | 6.3 | 0.178 | 0.200 | 11.0 |
| 9 | 0.290 | 0.288 | 0.7 | 0.182 | 0.195 | 6.7 |
| 10 | 0.282 | 0.288 | 2.1 | 0.189 | 0.200 | 5.5 |
| 11 | 0.568 | 0.573 | 0.9 | 0.430 | 0.410 | 4.9 |
| 12 | 0.570 | 0.550 | 3.6 | 0.435 | 0.413 | 5.3 |
| 13 | 0.668 | 0.713 | 6.3 | 0.500 | 0.470 | 6.4 |
| 14 | 0.660 | 0.764 | 14.0 | 0.495 | 0.494 | 0.2 |
| 15 | 0.250 | 0.270 | 7.4 | 0.160 | 0.190 | 16.0 |
| 16 | 0.273 | 0.264 | 3.4 | 0.179 | 0.180 | 0.6 |
| 17 | 0.177 | 0.145 | 22.0 | 0.131 | 0.124 | 5.6 |
| 18 | 0.178 | 0.164 | 8.5 | 0.129 | 0.124 | 4.0 |
| 19 | 0.181 | 0.183 | 1.1 | 0.136 | 0.124 | 9.7 |
| 20 | 0.180 | 0.169 | 6.8 | 0.133 | 0.124 | 7.3 |
| 21 | 0.273 | 0.280 | 2.5 | 0.195 | 0.193 | 1.0 |
| 22 | 0.275 | 0.282 | 2.5 | 0.197 | 0.194 | 1.6 |
| 23 | 0.350 | 0.366 | 4.4 | 0.269 | 0.262 | 2.7 |
| 24 | 0.361 | 0.360 | 0.3 | 0.270 | 0.263 | 2.7 |
| Std. Rel. Dev., % | | | ± 7.2 | | | ± 6.6 |

The spectrographic accuracy obtained should be comparable to the accuracy of chemical methods for the analysis of "fissium" alloy. Existing chemical methods were difficult and time consuming *(18)*. The spectrographic accuracy for the most part depended upon the reliability of the standards used and how well they resembled the sample, both physically and chemically.

In a reactor program that dealt with uranium, a radioactive element, the handling of this material was significant. This spectrographic procedure used a negligible amount of sample, and, as a result, insignificant amounts of waste products were encountered. Samples

Table V. Comparison of Spectrographic and Chemical Determinations of Zirconium in "Fissium" Alloy

| Sample No. | % ZIRCONIUM Spec. | Chem. | Rel. Dev., % |
|---|---|---|---|
| 1 | <1 | <1 | |
| 2 | <1 | <1 | |
| 3 | <1 | <1 | |
| 4 | <1 | <1 | |
| 5 | 2.46 | 2.44 | 0.8 |
| 6 | 2.31 | 2.46 | 6.1 |
| 7 | 2.38 | 2.44 | 2.5 |
| 8 | 2.43 | 2.62 | 7.3 |
| 9 | 2.80 | 2.60 | 7.7 |
| 10 | 2.62 | 2.60 | 0.8 |
| 11 | 5.97 | 5.45 | 9.5 |
| 12 | 5.85 | 5.32 | 9.9 |
| 13 | <1 | <1 | |
| 14 | <1 | <1 | |
| 15 | <1 | <1 | |
| 16 | <1 | <1 | |
| 17 | 1.63 | 1.59 | 2.5 |
| 18 | 1.80 | 1.56 | 15.0 |
| 19 | 1.73 | 1.62 | 6.8 |
| 20 | 1.70 | 1.58 | 7.6 |
| 21 | 2.77 | 2.60 | 6.5 |
| 22 | 2.60 | 2.61 | 3.8 |
| 23 | 3.80 | 3.49 | 8.9 |
| 24 | 3.68 | 3.50 | 4.6 |
| Std. Rel. Dev., % | | | ± 7.5 |

were returned to the originator in essentially the same condition, and no accountability problems were involved.

## Acknowledgment

The author thanks Frank L. Yaggee, Metallurgy Division, for the preparation of the spectrographic standards; Harold B. Evans, Special Materials Division, for chemical analysis of spectrographic standards; James K. Brody and Dr. Frank S. Tomkins, Chemistry Division for helpful discussions.

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# Identification of Barbiturates by X-ray Diffraction Powder Patterns of Their p-Nitrobenzyl Derivatives

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## Abstract

The identification of barbituric acids by the x-ray powder diffraction method is discussed from the practical point of view. Data are presented showing the advantage of preparing the *p*-nitrobenzyl derivative whenever identification of the isolated free acid is either doubtful or considered impossible. A detailed account of the experimental micro technique is given and the applicability of the technique to pharmaceutical products as forensic specimens is discussed.

## Introduction

Huang states "that it is not difficult to identify with the x-ray diffraction method a single pure substance or a specific modification, since each crystalline substance has its own characteristic pattern which is different from those of other crystalline substances" (*1*). Neglecting the very few known exceptions, there is no doubt that this reasoning applies to the group of twenty 5,5-disubstituted barbituric acids which are of clinical and toxicological importance. Therefore, despite the fact that some of the barbiturates are highly polymorphous in nature and may occur in up to 5 modifications (*2*), the use of an up-to-date index of the A.S.T.M. type (*3*) should make identification of an unknown barbiturate sample possible. For instance, Williams (*4*) showed by the x-ray diffraction method that crystallization from ether produces modification II of barbital, together with small amounts of modifications I and IV in reproducible proportions. Furthermore, in order to eliminate sorting out of the various modifications, an operation which increases in complexity with the size of the available index, one can standardize extraction and purification methods, as mentioned by Penprase and Biles (*5*), and obtain a set of standard films for identification of "unknowns". The method is simple; however, in practice with barbiturates, one encounters many difficulties. Crystallization conditions are not the only factors governing the appearance of a certain modification or mixture of modifications. Williams (*4*) reports that crystallization of aprobarbital (alurate) from ether does not yield reproducible patterns. Similar observations were made in this laboratory. This effect may be due to traces of impurities which according to Heiz (*6*) and Huang (*7*), have the tendency of rendering stable an unstable modification with some of the barbituric acids. Further, polymorphism is not the only difficulty presented by this class of compounds. Huang (*8*) and Hansen (*9*) studied mixed crystal formation in all the binary mixtures formed among 8 barbituric acids and published tables of line position and intensity shifts to be expected at several concentration ratios. Such mixed crystal formation can easily occur between barbituric acids and other organic compounds. Therefore, it is evident that no one system can offer positive identification in every case considered unless a prohibitive amount of data is accumulated to cover all possibilities.

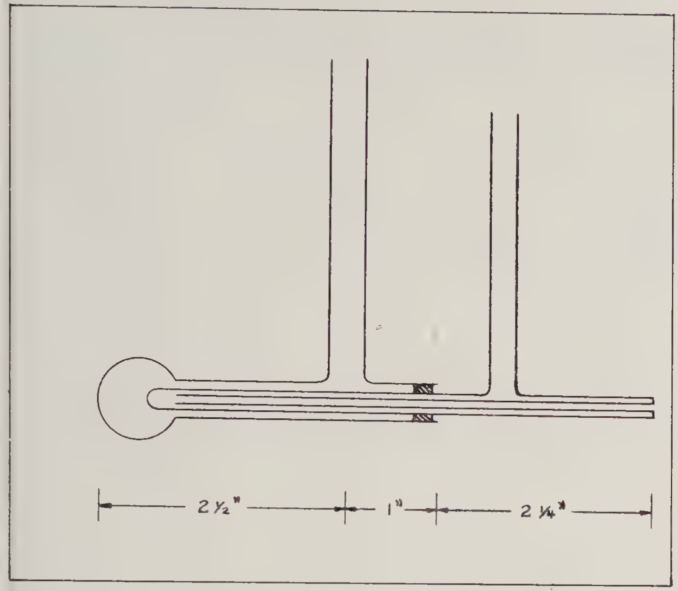

Fig. 1. Refluxing Apparatus

In this laboratory, research was initiated to eliminate the necessity of large accumulation of data for the identification of the barbituric acids. It was proposed to utilize a suitable derivative which would be easy to prepare on a micro scale, free from polymorphism, and have little tendency to form molecular compounds or mixed crystals with other components. Such a compound was found to be the *p*-nitrobenzyl derivative of the barbituric acids. No special investigation was made to show that these derivatives do not exhibit the above effects. However, indirect experimental proof may be derived from the fact that, in the course of this investigation, these derivatives were prepared in a number of different ways, and no change was ever observed in their crystallographic structures. This paper is intended to give an account of the experimental data showing the simplicity and the specificity of the method.

## Experimental

The methods of Lilliman (*10*) and of Castle and Poe (*11*) for the preparation of p-nitrobenzyl derivatives of barbituric acids were investigated. It was found that both methods gave excellent results at a micro scale with minor modifications, if the size of the refluxing apparatus was reduced. (Figure 1). This apparatus was made using pyrex tubings of 3, 5, 6, and 8 mm o.d. and the volume of the bulb was between 2-3 cc.

A mixture consisting of 1 mg of the barbituric acid, 1 mg of $Na_2CO_3$, 1.5 mg of *p*-nitrobenzyl chloride, 0.03 ml of $H_2O$, and 0.06 ml of ethyl alcohol was refluxed on a boiling bath for 1½ hrs. The *p*-nitrobenzyl derivative separated as a residue in the alcoholic solution. The contents of the flask were transferred to a filter. The residue was washed thoroughly with water to remove unreacted starting material and any monosubstituted *p*-nitrobenzyl derivative which may have formed. Sometimes, on washing the flask out with water, a fine white precipitate formed. It was also filtered off with the residue, as several x-ray diffraction patterns had shown that this fine white precipitate was in all cases a fraction of the *p*-nitrobenzyl derivative dissolved in the more concentrated alcoholic solution. The residue and filter paper were placed in an oven at 80°C and dried for 3 hrs.

The dried product was ground on a well-type microscope slide using a fine glass rod as pestle and observing the operation under a stereoscopic microscope. The ground specimen was either introduced into a 0.2 mm Lindemann glass capillary tube or mounted on a fine pyrex wire (0.1 mm diam., maximum) using household cement as suggested by Barnes (*12*). Diffraction patterns were obtained with Philips Debye-Scherrer cameras, diam. 114.83 mm, and Cu K$\alpha$ radiation.

## Results and Discussion

During the past few years, this laboratory has examined a number of barbiturate specimens. Figure 2 reports on an interesting court case involving a nembutal exhibit. The spectrum of the free acid isolated after several ether extractions, pattern *b*, could not be identified against that of the standard free acid on file, pattern *a*. The *p*-nitrobenzyl derivative of the isolated free acid was prepared; it can easily be seen by comparing patterns *c* and *d*, *p*-nitrobenzyl derivative of the standard and isolated free acid respectively, that unambiguous identification could now be made. Pattern *e* was obtained from the crude residue while pattern *d* from the same residue but following recrystallization. It was observed repeatedly that recrystallization was not required for the identification of an unknown barbituric acid sample by this method; therefore, it was normally not carried out in this work.

A commercial cyclopal sample was analyzed in the dry state by infrared spectrophotometry. The resulting spectrum, Figure 3, showed many discrepancies when compared with a standard spectrum. It was concluded that the discrepancies were due to either some unknown impurities or some polymorphic changes induced by the grinding process. An x-ray diffraction pattern of the commercial sample was also obtained, Figure 4*c*, and showed

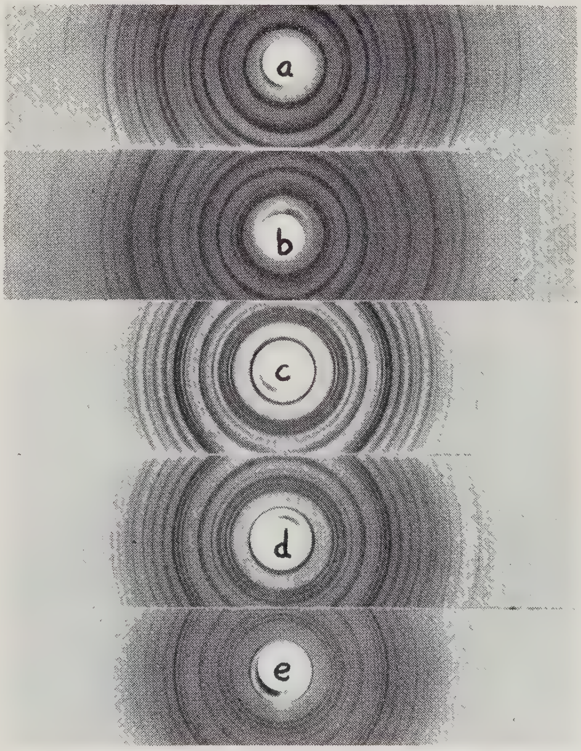

Fig. 2. Nembutal or Pentobarbital

*a*—standard free acid, *b*—isolated free acid, *c*—p.n.b. derivative of standard free acid, *d*—p.n.b. derivative of isolated free acid, *e*—same as *d* above, but not recrystallized

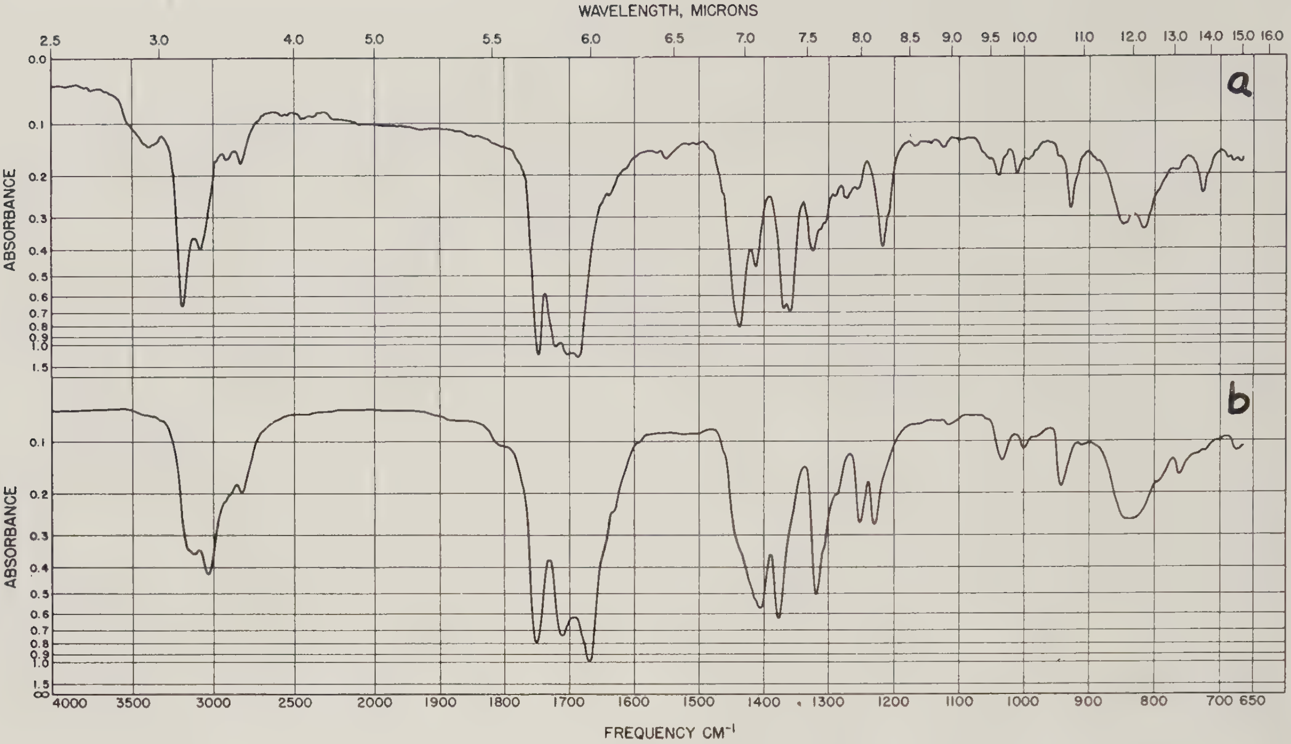

Fig. 3. Infrared Spectrum of Cyclopal. (KBr Pellet)

*a*—commercial free acid, *b*—standard free acid

no similarities with the corresponding free acid standard film, Figure 4*b*. The sample was dried to constant weight to eliminate the effect of absorbed humidity. Figure 4*d*, shows no change in the observed pattern. The sample was then dissolved in ether, and the ether evaporated. The resulting x-ray diffraction pattern, Figure 4*a*, was a perfect match with that of the standard, Figure 4*b*. It was also found that recrystallization from ether produced an infrared absorption spectrum identical to that of the standard. This work had proved that the discrepancies observed in the infrared spectrum of the commercial cyclopal sample with reference to the standard were due exclusively to polymorphism, not to some unknown impurities, and that the polymorphic changes had not been induced by the grinding process as in the cases reported by Cleverley and Williams (*13*). However, identification of the sample was readily achieved by preparing its *p*-nitrobenzyl derivative, as shown in Figure 4*e* and 4*f*.

Other cases on file, where difficulties were experienced in the identification of the free acid and where preparation of the *p*-nitrobenzyl derivative permitted positive identification, concern pentobarbital, secobarbital, amobarbital, phenobarbital, and butethal. They were similar in nature to those already reported, and will therefore not be described. However, it is felt that mention should be made of an effect which interfered for a while with the normal course of this work. Figure 5 will be used to illustrate the situation. The spectrum of the free acid isolated from a butethal sample, pattern *a*, could not be identified by comparison with that of the standard, pattern *b*. The *p*-nitrobenzyl derivative of the isolated free acid gave a pattern, Figure 5*c*, which differed from that of the standard, Figure 5*e*. Each line of the latter corresponded to a well resolved doublet in the former with the relative intensities being preserved. Identification of the submitted specimen as butethal was tentatively made. A literature survey indicated that nothing too specific has been written about the appearance of this effect. Taylor and Sincalir

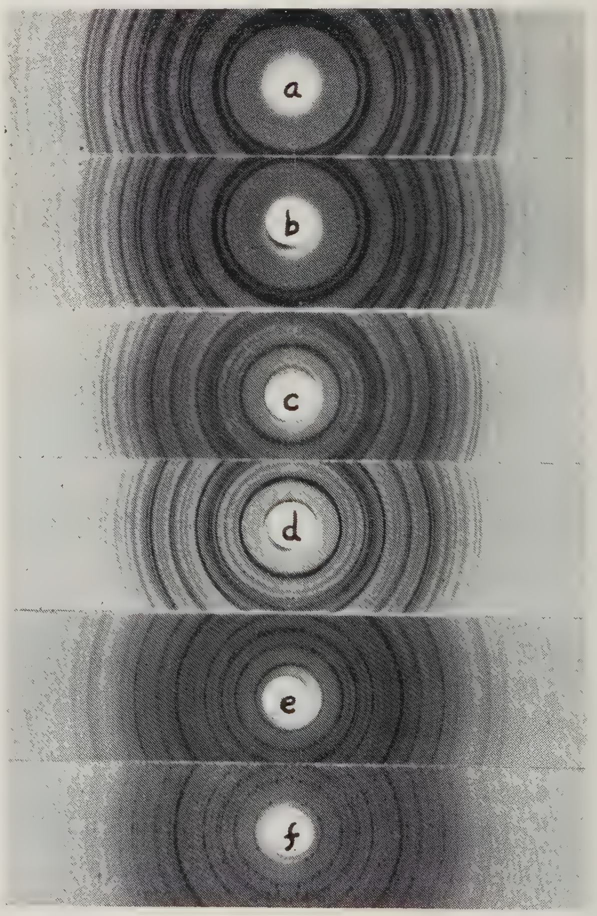

Fig. 4. Cyclopal

*a*—commercial free acid, *b*—standard free acid, *c*—commercial free acid, *d*—commercial free acid, dried to constant weight, *e*—p.n.b. derivative of standard free acid, *f*—p.n.b. derivative of commercial free acid

(*14*) have studied the effect of sample thickness on the line width of the observed pattern and drawn line profiles for various $\mu r$, where $\mu$ is the absorption coefficient and r the radius of the specimen. A short account of their findings is presented by Henry *et al.* (*15*). It is shown that as $\mu r$ is increased, doubling of the lines due to absorption from the center fraction of the specimen takes place for low values of $\Theta$. However, the results are not entirely consistent with the theory when the sample is coated on a fiber of larger density or greater absorption. The appearance of doublets, due to the relatively intense absorption within the solid core, takes place sooner than would be expected from optimum thickness consideration. This point is illustrated in Figure 6 which gives the patterns obtained from NaCl using Pyrex fibers of increasing diam. Even with a Pyrex fiber of 0.2 mm diam., a thickness commonly suggested (*16*), the two innermost lines are double while others indicate the presence of an unresolved doublet. In this laboratory, Pyrex fibers of maximum diam. of 0.1 mm are generally used. The spectrum of Figure 5*c*, which had been obtained inadvertently using a Pyrex fiber of 0.30 mm diam., was repeated with a fiber of 0.1 mm diam., Figure 5*d*. Figure 5*d* was now identical to Figure 5*e*.

The procedure outlined in this paper is the one normally followed in this laboratory. The free acid from the submitted sample is isolated through standard chemical procedure. An x-ray diffraction pattern of the free acid is obtained. If identification is not possible or is doubtful at at this stage, the *p*-nitrobenzyl derivative is formed and its x-ray diffraction pattern is obtained. The derivative may be easily prepared with as little as 1 mg of the acid and the x-ray powder diffraction data for the *p*-nitrobenzyl derivatives of 20 clinically important barbituric acids are available (*17*). So far, none of the cases considered, including pharmaceutical products (pills or capsules) as forensic exhibits, failed to yield positive criteria of identification when processed in this way. With enteric coated tablets, it was found preferable to scrape the enteric coating before isolation of the free acid; otherwise, some coloring material would follow repeated ether extractions and interfere. Thus far, the work of this laboratory has been restricted to pharmaceutical samples. However, it is planned to apply the method to a number of toxicological samples where interference from several impurities of metabolic origin is known to cause serious difficulties in conventional identification methods.

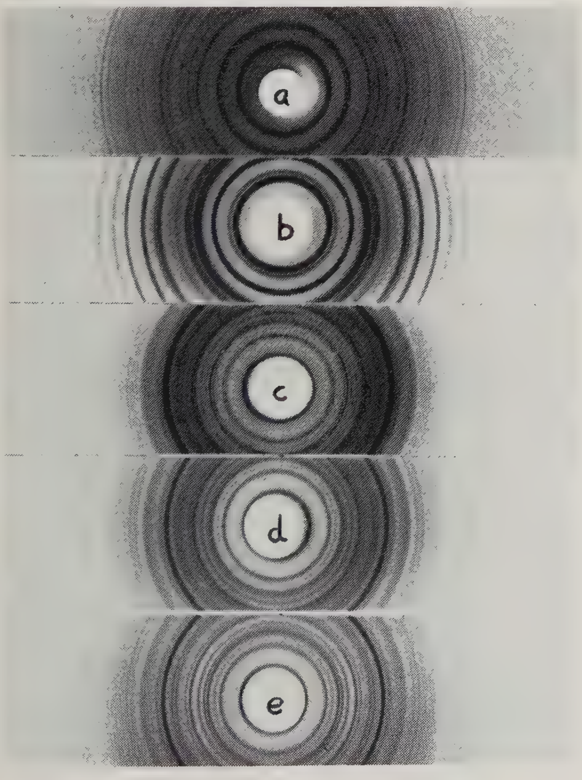

Fig. 5. Butethal or Neonal

*a*—standard free acid, *b*—isolated free acid, *c*—p.n.b. derivative of isolated free acid, 0.30 mm Pyrex fiber mount, *d*—p.n.b. derivative of isolated free acid, 0.10 mm Pyrex fiber mount, *e*—p.n.b. derivative of standard free acid, 0.20 mm capillary tube .

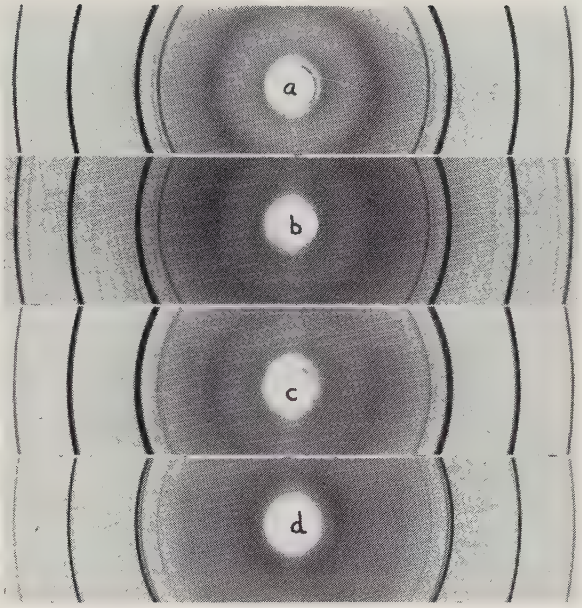

Fig. 6. Study of the Effect of Pyrex Fiber Diameter on Line Profile

Sample—NaCl, *a*—0.1 mm diam, *b*—0.2 mm diam., *c*—0.3 mm diam., *d*—0.5 mm diam.

## Acknowledgement

The authors are indebted to Dr. L. Levi for helpful discussions.

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# Mass Spectrometry of Some High Molecular Weight Aliphatic Acids and Their Methyl Esters. Analysis of Nonanoic and 2-Ethylheptanoic Acid Mixtures[†]

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## Abstract

The mass spectra are given of nonanoic, 2-ethylheptanoic, 2,5-diethylhexanedioic, 2-ethyloctanedioic, and decanedioic acids with the methyl esters of these acids. Quantitative methods are described for the analysis of nonanoic and 2-ethylheptanoic acid mixtures as well as mixtures of the respective methyl esters. Data are given for the precision and accuracy of the methods. By using a diazomethane esterification procedure, the C-9 monobasic and C-10 dibasic acids were quantitatively converted to their methyl esters.

## Introduction

"Isosebacic"[*] acid is prepared by dimerizing butadiene with sodium to form disodiooctadiene (*1*). The slurry of organometallics is carbonated to form the sodium salts of the unsaturated acids which are hydrogenated to a mixture of the sodium salts of 2,5-diethylhexanedioic acid, 2-ethyloctanedioic acid and decanedioic acid. Small amounts of nonanoic and 2-ethylheptanoic acids are produced as by-products.

Mass spectroscopy and gas chromatography are two analytical techniques which can be adapted to the analysis of a mixture of these acids. The mass spectra of these acids and their methyl esters are reported here. In addition, analytical data are given for mixtures of the $C_9$ acids and their methyl esters. Data on the three $C_{10}$ acids and their methyl esters show that mass spectrometry could be utilized in the analysis of a mixture of these acids and the $C_9$ acids or esters of these acids.

The application of mass spectrometry to qualitative and quantitative analysis has been reviewed (*2-4*). Happ and Stewart (*5*) investigated the mass spectra of low molecular weight aliphatic acids. By use of $C^{13}$ carboxyl labeled n-butyric acid they proved that the peak at mass 60 for n-butyric acid is due to breaking the carbon bond between the $\alpha$ and $\beta$ carbon atoms with transfer of hydrogen from the remaining fragment. Cracking patterns have been reported on high molecular weight alcohols (*6*), long chain esters (*7-10*), saturated aliphatic aldehydes (*11*) and saturated aliphatic ethers (*12*). Cracking patterns obtained for the $C_9$ and $C_{10}$ acids and esters show a strong resemblance to the aldehydes and ethers in that beta carbon cleavage is quite prominent.

## Experimental

The $C_9$ acids used in this study were prepared by vacuum fractional distillation of impure materials. The $C_{10}$ acids were also separated by vacuum fractional distillation. These latter fractions still contained small amounts of impurities which were removed by repeated crystallization from toluene. Gas chromatographic analysis of methyl esters of the acids showed the following purities: nonanoic, 99.7, 2-ethylheptanoic, 99.6, 2,5-diethylhexanedioic, 99.8, 2-ethyloctanedioic, 99.9, and decanedioic, 99.8%. Physical data on these compounds have been published (*13*).

The methyl esters were prepared in quantity by acid catalyzed esterification with methyl alcohol. A second method for smaller amounts (0.5-2 g) involved reaction of the acid in ether solution with diazomethane. The diazomethane was prepared by the method of de Boer and Backer (*14*) and the reaction between diazomethane and the acids was carried out in anhydrous ether. The esters used for mass spectrometry were found by gas chromatographic analysis to have the following purities: methyl nonanoate, 99.9, methyl 2-ethylheptanoate, 99.8, dimethyl 2,5-diethylhexanedioate, 99.9, dimethyl 2-ethyloctanedioate 99.9, and dimethyldecanedioate, 99.8%.

The spectra were obtained on a General Electric Mass Spectrometer, Model GE 1-28508B. This instrument is a Nier type 60° single focusing instrument with a 6-in. radius of curvature. With this instrument the spectrum is obtained by varying the magnetic field. The input resistors of both preamplifiers were changed so as to increase the sensitivity of the instrument by a factor of two. A general Electric heated molecular leak was used.

The operating conditions of the mass spectrometer were as follows: accelerating potential, 2000 v, ionizing

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[†] This paper was presented at the Tenth Annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1959.

[*] Registered Trade Mark of U. S. Industrial Chemicals Co., Division of National Distillers and Chemical Corporation.

TABLE I. NORMALIZED MASS SPECTRA OF SOME $C_9$ MONOBASIC AND $C_{10}$ DIBASIC ACIDS

| *Compound* | *Nonanoic Acid* | *2-Ethyl heptanoic Acid* | *2,5-Diethyl hexanedioic Acid* | *2-Ethyl octanedioic Acid* | *Decane dioic Acid* |
|---|---|---|---|---|---|
| *Mol. Wt.* | *158* | *158* | *202* | *202* | *202* |
| M/e | | | | | |
| 27 | 13.1 | 8.7 | 9.7 | 16.0 | 11.5 |
| 28 | 3.9 | 2.1 | 2.6 | 5.0 | 4.7 |
| 29 | 16.9 | 12.1 | 11.4 | 19.3 | 12.4 |
| 30 | | | | 1.1 | |
| 31 | 1.3 | | 1.4 | 3.2 | 2.6 |
| 37 | | | | 1.0 | |
| 38 | | | | | |
| 39 | 11.8 | | 11.0 | 17.5 | 15.3 |
| 40 | 20.2 | 1.4 | 2.3 | 3.6 | 3.1 |
| 41 | 38.1 | 24.7 | 37.8 | 52.0 | 45.8 |
| 42 | 10.4 | 4.3 | 6.9 | 15.3 | 14.3 |
| 43 | 38.5 | 24.3 | 14.3 | 32.2 | 27.2 |
| 44 | 1.7 | 1.5 | 1.9 | 4.3 | 5.8 |
| 45 | 11.2 | 8.9 | 18.1 | 24.2 | 24.3 |
| 46 | | 1.5 | | 1.1 | |
| 51 | | | 1.2 | 1.0 | 1.3 |
| 52 | | | | 1.7 | |
| 53 | 3.1 | 2.4 | 5.6 | 1.1 | 6.1 |
| 54 | 3.1 | | 2.5 | 7.2 | 6.1 |
| 55 | 35.9 | 19.3 | 49.4 | 100.0 | 100.0 |
| 56 | 11.3 | 4.5 | 17.2 | 18.7 | 17.0 |
| 57 | 57.8 | 16.3 | 11.7 | 17.3 | 12.8 |
| 58 | 3.0 | | | 3.2 | 1.9 |
| 59 | 3.6 | 2.6 | 5.8 | 8.9 | 8.3 |
| 60 | 100.0 | 3.2 | 2.5 | 2.1 | 48.7 |
| 60.7 | | 1.3 | | | |
| 61 | 6.4 | | | | 5.5 |
| 65 | | | | 1.5 | 1.3 |
| 66 | | | | 1.0 | 1.0 |
| 67 | 2.4 | 1.0 | 5.2 | 10.8 | 11.5 |
| 68 | 2.5 | 1.2 | 6.6 | 9.1 | 13.6 |
| 69 | 18.1 | 8.0 | 100.0 | 52.8 | 43.9 |
| 70 | 6.5 | 3.5 | 33.3 | 35.5 | 15.8 |
| 71 | 3.3 | 9.1 | 6.2 | 11.4 | 6.6 |
| 72 | | | 1.6 | 3.2 | |
| 73 | 89.7 | 86.1 | 64.7 | 94.3 | |
| 74 | 8.0 | 4.3 | 3.4 | 5.3 | |
| 75 | | | | 1.1 | |
| 77 | | | | 1.7 | |
| 79 | | | 1.5 | 3.7 | 6.1 |
| 80 | | | | 1.1 | 9.2 |
| 81 | 2.3 | | | 11.3 | 13.7 |
| 82 | | | 3.0 | 7.2 | 9.4 |
| 83 | 8.2 | 3.5 | 16.2 | 27.0 | 46.1 |
| 84 | 5.4 | 3.3 | 5.2 | 17.6 | 52.1 |
| 85 | 1.3 | 1.0 | 2.9 | 4.9 | 5.9 |
| 86 | | | 1.7 | 2.1 | 1.9 |
| 87 | 12.1 | 16.8 | 10.8 | 10.2 | 10.5 |
| 88 | 7.5 | 100.0 | 63.8 | 71.6 | 15.4 |
| 89 | | 4.7 | 3.1 | 3.8 | 1.1 |
| 91 | | | | 1.1 | 1.6 |
| 93 | | | | | 2.9 |
| 94 | | | | 2.6 | 4.7 |
| 95 | | | 3.1 | 3.2 | 8.5 |
| 96 | 5.0 | | 2.8 | 7.9 | 12.3 |
| 97 | 3.4 | 1.4 | 19.8 | | 41.9 |
| 98 | 11.5 | | 5.8 | 59.9 | 87.5 |
| 99 | 3.8 | | 4.0 | 26.8 | 9.1 |
| 100 | | | 6.6 | 7.2 | 5.3 |
| 101 | 7.9 | 35.3 | 25.7 | 12.6 | 10.4 |
| 102 | | 2.5 | 1.7 | 14.2 | |
| 103 | | | | 1.5 | |
| 108 | | | | 1.5 | 1.4 |
| 109 | | | | | 7.3 |
| 110 | | | 3.5 | 5.5 | 1.5 |
| 111 | 1.1 | | 5.2 | 6.6 | 5.1 |
| 112 | | | 10.2 | 7.2 | 9.9 |
| 113 | | | 11.2 | 10.6 | 11.6 |
| 114 | | | 2.7 | 4.6 | 17.7 |
| 115 | 19.9 | | 1.0 | 3.0 | 4.2 |
| 116 | 1.5 | | 14.9 | 4.0 | 2.4 |
| 117 | | | 1.1 | 1.7 | 5.4 |
| 121 | | | | | 1.1 |
| 122 | | | | 2.1 | 2.1 |
| 123 | | | | 1.3 | 3.5 |
| 124 | | | | 2.4 | 2.4 |
| 125 | | | | 2.8 | 2.7 |
| 126 | | | 1.1 | 10.2 | 5.0 |
| *Mol. Wt.* | *158* | *158* | *202* | *202* | *202* |
| 127 | | | | 1.7 | 41.0 |
| 128 | | | 4.4 | 2.8 | 4.0 |
| 129 | | | 22.2 | 14.4 | 2.1 |
| 130 | | | 2.2 | 5.3 | 4.8 |
| 131 | | | | | 3.1 |
| 132 | | | | | 1.2 |
| 138 | | | | 12.5 | 4.9 |
| 139 | | | 1.4 | 27.6 | 34.4 |
| 140 | | | 7.6 | 6.4 | 4.1 |
| 141 | | | 4.3 | 1.5 | 5.0 |
| 142 | | | 1.0 | 1.3 | 1.4 |
| 143 | | | 1.4 | 1.9 | |
| 144 | | | 1.2 | 8.6 | 6.7 |
| 145 | | | | 1.1 | |
| 153 | | | | 1.1 | |
| 157 | | | 1.1 | 1.1 | 2.9 |
| 158 | 1.7 | 0.7 | 1.7 | 8.3 | |
| 159 | | | 2.5 | 2.6 | |
| 160 | | | 1.3 | 1.4 | |
| 168 | | | | 22.3 | 16.9 |
| 169 | | | 2.3 | 2.8 | 2.0 |
| 187 | | | 1.0 | | 1.8 |
| Sensitivity[a] | 572 (M/e 60) | 556 (M/e 88) | 119 (M/e 69) | 235 (M/e 55) | 35.8 (M/e 55) |

[a] Sensitivity as Sensitivity Coefficient (Chart divisions/μl)

currents 16μamp for the acids and 11 μamp for the methyl esters. An ionizing potential of 75 v was used, while the temperature of the ion source was maintained as 200°C.

The heated sample system was of the O'Neal and Wier design (*15*) with the 3 l vapor reservoir connected to a molten gallium pump-out valve operated with a permanent magnet.

Sample volumes were measured in the early studies by use of a microdipper pipet (*16*), but this was discarded in favor of a micro delivery syringe†. The syringe was calibrated using mercury and was found to have a dead space of 1 μl when it was used as a delivery pipet. Two μl samples were used for the cracking patterns of the acids and 3 μl samples for the esters except dimethyldecanedioate for which a 4 μl sample was used.

Temperatures for the sample system were as follows: 160°C for the $C_9$ acids, 180°C for the $C_{10}$ acids and 200°C for all the methyl esters. Even though the lower temperatures used for the acids gave adequate results, a temperature of 200°C would have given somewhat more satisfactory results because of the increase in vapor pressure.

Since polar compounds are strongly adsorbed by glass, it was not surprising to find that the $C_9$ acids were highly adsorbed on the walls of the analyzer tube and sample system. Several methods were tried in order to condition the instrument to the sample under study. The ideal material to use for removing a sample from the walls of a container would be a substance that is more polar than the compound under study and also one that has a low mass number. Among others, water and formic acid were used as desorbing agents, but it was found that three admissions and pump outs of the $C_9$ acid samples conditioned the instrument effectively. Six sample admissions and pump outs of the $C_{10}$ acids were required to desorb the previous sample and condition the instrument. The methyl esters of both $C_9$ and $C_{10}$ acids could be run after pump out times of 20 min between sample admissions without the need of several sample introductions to condition the instrument.

## Results

Tables I and II summarize the cracking patterns of nonanoic, 2-ethylheptanoic, 2,5-diethylhexanedioic, 2-

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†Cat. No. 705, Hamilton Co., Whittier, Calif.

TABLE II. NORMALIZED MASS SPECTRA OF METHYL ESTERS OF SOME $C_9$ MONOBASIC AND $C_{10}$ DIBASIC ACIDS

| Compound | Methyl Nonanoate | Methyl 2-Ethylheptanoate | Dimethyl 2,5-Diethylhexanedioate | Dimethyl 2-Ethyloctanedioate | Dimethyl Decanedioate |
|---|---|---|---|---|---|
| *Mol. Wt.* | *172* | *172* | *230* | *230* | *230* |
| M/e | | | | | |
| 15 | 2.4 | 5.9 | 6.3 | 7.4 | 9.5 |
| 27 | 7.5 | 19.5 | 7.0 | 9.1 | 13.5 |
| 28 | 2.8 | 5.2 | 3.1 | 4.3 | 9.0 |
| 29 | 10.3 | 26.1 | 6.8 | 13.3 | 19.6 |
| 31 | 1.0 | 1.2 | 1.0 | 1.9 | 3.5 |
| 39 | 5.9 | 13.4 | 6.8 | 11.0 | 12.7 |
| 40 | 1.3 | 4.4 | 1.5 | 2.4 | 3.1 |
| 41 | 20.3 | 46.5 | 34.4 | 38.7 | 51.7 |
| 42 | 6.2 | 8.7 | 5.8 | 9.8 | 15.5 |
| 43 | 30.2 | 42.6 | 6.9 | 21.7 | 55.0 |
| 44 | 2.3 | 1.6 | | 1.4 | 3.0 |
| 45 | 1.7 | 1.4 | 5.5 | 7.6 | 7.6 |
| 53 | 1.7 | 4.4 | 4.0 | 5.4 | 4.9 |
| 54 | 1.3 | 1.7 | 1.8 | 4.5 | 4.8 |
| 55 | 19.4 | 34.9 | 40.2 | 73.4 | 100.0 |
| 56 | 4.0 | 8.9 | 7.9 | 10.0 | 11.6 |
| 57 | 11.4 | 37.6 | 3.7 | 6.5 | 9.0 |
| 58 | | 1.8 | | | 1.1 |
| 59 | 12.8 | 19.7 | 29.5 | 38.5 | 42.9 |
| 60 | | | | 1.5 | 1.7 |
| 62 | | | 1.0 | | |
| 67 | 1.4 | | 3.7 | 8.7 | 9.1 |
| 68 | 1.3 | 1.5 | 3.3 | 4.3 | 6.1 |
| 69 | 7.7 | 1.6 | 56.9 | 50.5 | 34.8 |
| 70 | 1.5 | 13.0 | 12.9 | 14.5 | 7.6 |
| 71 | 4.5 | 6.1 | 2.9 | 4.6 | 3.4 |
| 72 | | 23.4 | | 1.3 | |
| 73 | 2.1 | 1.5 | | 10.6 | 9.5 |
| 74 | 100.0 | 3.9 | 9.6 | 26.3 | 86.7 |
| 75 | 7.7 | 5.5 | | 1.6 | 5.5 |
| 79 | | | 1.0 | 2.3 | 3.9 |
| 80 | | | | | 4.5 |
| 81 | 1.2 | | 5.2 | 9.0 | 10.4 |
| 82 | | | 1.7 | 3.8 | 5.1 |
| 83 | 3.3 | | 8.2 | 13.1 | 28.1 |
| 84 | 3.3 | 5.4 | 1.3 | 7.1 | 38.8 |
| 85 | | 2.9 | 1.4 | 3.5 | 4.4 |
| 87 | 46.5 | 100.0 | 59.0 | 87.1 | 30.0 |
| 88 | 4.8 | 5.8 | 4.5 | 6.2 | 4.2 |
| 93 | | | | 1.9 | 1.4 |
| 94 | | | | 2.2 | 3.4 |
| 95 | | | 1.8 | 7.8 | 7.3 |
| 96 | | | 1.2 | 10.6 | 8.7 |
| 97 | 2.0 | 2.0 | 4.8 | 44.4 | 34.5 |
| 98 | 1.3 | 1.5 | 1.2 | 12.5 | 45.5 |
| 99 | | | 2.1 | 1.2 | 4.9 |
| 100 | | | | 1.4 | |
| 101 | 4.7 | 16.3 | 7.3 | 8.6 | |
| 102 | 1.4 | 98.9 | 100.0 | 100.0 | 7.0 |
| 103 | | 5.4 | 5.8 | 5.8 | 1.9 |
| 107 | | | | | 1.2 |
| 108 | | | | | 3.9 |
| 110 | | | 3.5 | 4.0 | 2.3 |
| 111 | | | 5.3 | 5.3 | 5.5 |
| 112 | | | 15.2 | 6.9 | 8.2 |
| 113 | | | 2.4 | 3.2 | 4.5 |
| 114 | | 4.1 | 4.4 | 4.2 | 2.1 |
| 115 | 1.3 | | 4.7 | 10.0 | 1.6 |
| 116 | | 24.1 | 7.5 | 7.8 | 6.8 |
| 117 | | 2.3 | | 1.5 | |
| 121 | | | | | 1.7 |
| 122 | | | | | 6.9 |
| 123 | | | | 4.2 | 1.7 |
| 124 | | | | | 1.8 |
| 125 | | | | 1.4 | 5.0 |
| 126 | | | | 1.6 | 37.6 |
| 127 | | | | 5.8 | 3.9 |
| 128 | | | | | 1.5 |
| 129 | 5.8 | | 1.9 | 2.4 | |
| 130 | | 2.3 | | 1.7 | 1.4 |
| 131 | | | 26.9 | 18.1 | 18.1 |
| 132 | | | 2.1 | 1.6 | 1.6 |
| 139 | | | | 8.5 | 2.0 |
| 140 | | | 4.6 | 24.3 | |
| 141 | 7.0 | | 8.6 | 23.0 | |
| 142 | | | | 2.5 | |
| 143 | 4.6 | 3.3 | 4.4 | 2.5 | |
| 144 | | | 12.3 | 4.4 | |
| 145 | | 5.9 | 1.2 | 1.1 | |
| 146 | | 7.9 | | | 2.1 |
| 150 | | | | | 3.0 |
| 151 | | | | | 1.3 |
| 153 | | | | 1.0 | |
| 157 | | | 1.9 | | |
| 158 | | | | 1.5 | |
| 159 | | | | 12.9 | 20.7 |
| 160 | | | | 1.3 | 2.7 |
| 168 | | | | 24.6 | 15.1 |
| 169 | | | | 2.9 | 2.6 |
| 171 | | | 13.5 | | |
| 172 | 0.7 | 0.4 | 14.8 | 10.7 | 1.9 |
| 173 | | | 1.6 | 25.2 | |
| 174 | | | | 2.7 | |
| 200 | | | 1.1 | 2.9 | 1.0 |
| 201 | | | 5.5 | 4.0 | 5.6 |
| 202 | | | | | 2.6 |
| 204 | | | 1.0 | 2.3 | |
| Sensitivity[a] | 1082 (M/e 74) | 566 (M/e 102) | 816 (M/e 103) | 508 (M/e 103) | 550 (M/e 55) |

[a] Sensitivity as Sensitivity Coefficient (Chart division/μl)

ethyloctanedioic and decanedioic acids as well as the methyl esters of these acids. All spectra were determined in duplicate and the data recorded in Tables I and II are the averages of the duplicates.

It was found that the most prominent fragment for nonanoic M/e 60($C_2H_4O_2^+$) and 2-ethylheptanoic M/e 88($C_4H_8O_2^+$) acids was produced by splitting the bond beta to the carbonyl. The mechanism for this cleavage was established by Happ and Stewart *(5)*. Similar behavior in the mass spectrometric analysis of aliphatic ethers *(12)* and aliphatic aldehydes *(11)* has been reported.

The most prominent fragments for 2,5-diethylhexanedioic, 2-ethyloctanedioic and decanedioic acids are M/e 69($C_5H_9^+$), M/e 55($C_4H_7^+$), and M/e 55($C_4H_7^+$), respectively. This suggests that for high molecular weight oxygenated compounds the hydrocarbon portion of the molecule will give rise to the most abundant ion fragment. Ryhage and Stenhagen found this to be the case for dimethyloctanedioate *(17)*.

For the methyl esters, the most intense fragment for methyl nonanoate is M/e 74($C_3H_6O_2^+$). This fragment results from the splitting at the beta carbon atom. For methyl-2-ethylheptanoate the fragment, M/e 87($C_4H_7O_2^+$), represents the most prominent fragment while the fragment, M/e 102($C_5H_{10}O_2^+$), has an intensity close to that of the prominent fragment. This fragment (M/e 102) is formed by beta carbon splitting.

The most prominent fragments for dimethyl 2,5-diethylhexanedioate and dimethyl-2-ethyloctanedioate are found to be at a mass of 102($C_5H_{10}O_2^+$). This ion is likewise formed from β carbon splitting. The most prominent fragment for dimethyldecanedioate is 55($C_4H_7^+$). Ryhage and Stenhagen *(17)* found the same fragment in the methyl esters of high molecular straight chain dibasic acids. The ion fragments and reaction mechanisms for methyl esters of straight chain dibasic acids have been determined *(7-10, 17)*.

All fragments, with the exception of the parent fragment, having a relative intensity of less than one percent were not included in Tables I and II.

TABLE III. ANALYSIS OF $C_9$ ACIDS

| Mixture No. | Nonanoic Acid Actual | Nonanoic Acid Found | 2-Ethylheptanoic Acid Actual | 2-Ethylheptanoic Acid Found |
|---|---|---|---|---|
| 1 | 4.8 | 4.4, 4.6 | 95.2 | 95.6, 95.4 |
| 2 | 44.5 | 43.9, 45.0 | 55.5 | 56.1, 55.0 |

Table IV. Analysis of the Methyl Esters of $C_9$ Acids

| Mixture No. | Methyl Nonanoate Actual | Methyl Nonanoate Found | Methyl 2-Ethylheptanoate Actual | Methyl 2-Ethylheptanoate Found |
|---|---|---|---|---|
| 1 | 91.5 | 91.2 | 8.5 | 8.8 |
| 2 | 78.4 | 77.7 | 21.6 | 22.2 |
| 3 | 53.4 | 52.9 | 46.6 | 47.1 |
| 4 | 27.8 | 27.9 | 72.2 | 72.1 |

Data for analysis of mixtures of $C_9$ acids are given in Table III. The peaks used in the analysis of the $C_9$ acids were M/e of 60 for nonanoic acid and M/e of 88 for 2-ethylheptanoic acid. The accuracy in the analysis of the 2 $C_9$ acids is 0.69% absolute error while the standard deviation for 7 determinations of mixtures of the acids is ± 0.90%. Mixtures of the methyl esters of the 2 $C_9$ acids were analyzed. Data from these analyses may be found in Table IV. The peaks chosen for the analysis of this mixture were M/e of 73 for methylnonanoate and M/e of 102 for methyl 2-ethylheptanoate. Analyses of mixtures of the 2 esters have an average absolute error of 0.40% while the standard deviation for 4 determinations of mixtures of the 2 esters is ± 0.53%.

Based on the data obtained on the methyl esters of the $C_{10}$ acids it is obvious that mixtures of these 3 esters could be analyzed by mass spectrometry. Although unique peaks are not available for the analysis of mixtures of all 5 acids or esters the stability of the cracking patterns indicates that routine analyses are possible by the use of simultaneous equations.

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# Pressure-Broadening Effects on Infrared Peak Intensities of Hydrocarbons

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## Abstract

The pressure-broadening effects of one atmosphere of air or of carbon dioxide on various infrared bands of hydrocarbons have been investigated. Large pressure-broadening effects are shown by ethylene at 10.52 microns and acetylene at 3.1 and 13.7 microns, moderate effects by acetylene at 7.4 microns and propylene at 10.95 microns, and small effects by 1-butene at 10.85 microns, trans-2-butene at 10.375 microns, and benzene at 9.50 microns. The variation of absorbance at several of the infrared absorption maxima of ethylene and acetylene has been investigated using varying partial pressures of air or carbon dioxide at fixed partial pressures of the 2 hydrocarbons.

## Introduction

The quantitative infrared analysis of gas mixtures resulting from combustion processes or atmospheric pollution usually is done at atmospheric pressures. The effects of the partial pressures of nonabsorbing gases on the absorption band of a particular component being analyzed may be of considerable significance.

The appreciable effects of varying the pressure of various nonabsorbing gases in the gas cell on the absorbance at the absorption band maxima of given polar or nonpolar gaseous species have been known for many years. In comparatively recent years there have been several relevant publications (*1-7*). These investigations point out a number of empirical generalities that may be used to advantage in analytical applications. However, some gaps exist in the information as to the magnitude of the pressure-broadening effects on two- through four-carbon hydrocarbons. Also it is not clear whether or not pressure-broadening effects might be observable for some absorption bands of five-carbon and larger molecules in the gaseous state. Furthermore, few of the available data have been obtained with the partial pressures of the absorbing gas below 20 mm Hg. Finally, the magnitude of the differential effects of substituting a higher molecular weight gas such as $CO_2$ for lower molecular weight nonabsorbing gases does not appear to have been investigated in detail. It appeared that the substitution of 10 - 15% $CO_2$ for oxygen in combustion mixtures might have a small but significant pressure-broadening effect. The present investigation was initiated to gain some further information on these problems.

## Experimental

The hydrocarbons used were Matheson instrument, C.P. grade, or Phillips 99+ mole % gases and reagent grade benzene. These materials were used as received.

The infrared data were obtained with a Beckman IR-4 infrared spectrophotometer using sodium chloride optics and standard slit-widths. Peak absorbancies were obtained either with the wavelength drive stopped at the wavelength of the peak maxima or with a scanning speed of 0.02 microns per min.

The absorption cell used was a Perkin-Elmer multiple-pass cell fixed at 1.25 meters optical path length. The windows on the cell were silver chloride plano-convex lenses.

In the preliminary measurements, which included the measurements of the broadening of several of the ethylene and acetylene peaks at various partial pressures of air and $CO_2$, the cell was evacuated down to about 0.2 mm Hg once and then filled with hydrocarbon gas. The mercury manometer was so situated that the gas volume in one arm of the manometer was included in the total volume measured.

During the later work in which the pressure-broadening was measured with the addition of one atmosphere of air or $CO_2$, the absorption cell was filled by a different procedure than that used in the preliminary measurements. In these later determinations, the cell was pumped down and filled with the hydrocarbon under investigation several times before finally adjusting the partial pressure of the gas. This procedure should insure the absence of air or carbon dioxide in the cell or inlet lines. The hydrocarbon gas was pumped out until the partial pressure was about that desired as judged by the absorbance readings, the vacuum pump was cut out of the system, and the pressure read on a McLeod gauge. The portion of the system containing the McLeod gauge and U-type mercury manometer was then cut off. Finally, the inlet line was disconnected. The bottom of the valve leading to the cell was flushed with $CO_2$ prior to pressure broadening with this gas.

The benzene was vaporized into the infrared cell from a small liquid reservoir containing the benzene until an appropriate pressure was reached.

## Results

Pressure-broadening by both air and $CO_2$ increases the intensities of the maxima of the carbon-hydrogen bending vibration of ethylene at 10.52 microns and the P branch of the parallel band of acetylene at 7.63 microns from 300 - 500% as shown in Table I. The results indicate that the intensity of the carbon-hydrogen bending vibration of propylene at 10.95 microns is increased 20 - 35% by one atmosphere of air or $CO_2$. The intensity of the maxima of the corresponding carbon-hydrogen bending vibration of trans-2-butene at 10.38 microns is very slightly increased by air or $CO_2$ (Table I). The data given show that the broader peak at 10.85 microns of 1-butene is increased in intensity by about the same amount as the sharper band of trans-2-butene.

The absorption maxima of ethylene, propylene, 1-butene, and trans-2-butene are all increased in intensity very slightly by one atmosphere of $CO_2$ compared with one atmosphere of air, as may be seen Table II. However, the maximum of the 7.63-micron band of acetylene is increased in intensity appreciably more by one atmosphere of $CO_2$ than by one atmosphere of air.

TABLE I. PRESSURE-BROADENING DATA ON VARIOUS INFRARED BANDS OF HYDROCARBONS USING ONE ATMOSPHERE OF THE BROADENING GAS

| *Compound* | *λ, μ* | *Pressure range, mm* | *Broadening Gas* | *% increase in intensity* |
|---|---|---|---|---|
| Ethylene | 10.52 | 0.63, 1.00 | air | 470—500 |
| | | | $CO_2$ | 480—550 |
| Acetylene | 7.63 | 5-20 | air | 310—440 |
| | | | $CO_2$ | 410—500 |
| Propylene | 10.95 | 0.45-1.5 | air | 20—30 |
| | | | $CO_2$ | 20—37 |
| 1-Butene | 10.85 | 1.0, 3.0 | air | 1 |
| | | | $CO_2$ | 4 |
| *trans*-2-Butene | 10.37 | 0.70, 1.92 | air | 1 |
| | | | $CO_2$ | 4 |
| Benzene | 9.50 | 2.3-10.0 | air | 12—14 |
| | | | $CO_2$ | 13—14 |

It might not be expected that absorption bands of as large a molecule as benzene would undergo pressure-broadening. However, pressure-broadening has been observed for the 14.8 micron band (6). The results listed in Table I also indicate that the rather sharp vibrational band of benzene at 9.50 microns increases in intensity by 12 - 14% at partial pressures of 2.3, 5.0, and 10.0 mm of benzene, using one atmosphere of air or $CO_2$ to cause pressure-broadening. No significant difference was observed in 'the pressure-broadening of the 9.50-micron band of benzene by $CO_2$ when compared to air.

Small partial pressures of air or $CO_2$ cause marked increases in the intensities of the ethylene band at 10.5 microns and acetylene band at 13.7 microns, as may be seen in Figures 1-3. The intensity of the 10.5-micron band of ethylene is about doubled when 20 mm of air are added to one mm of ethylene. The 13.7-micron band of acetylene is almost tripled in intensity by 20 mm of $CO_2$ or air.

The variation in the absorbancies of the maxima of the 3.1-, 7.4-, and 13.7-micron bands of acetylene is given in Figure 2 as a function of the partial pressure of $CO_2$. The 13.7 micron band is much more sensitive to pressure-broadening by $CO_2$ than is the carbon-hydrogen stretching vibration at 3.1 microns, which in turn is more sensitive to pressure-broadening than is the 7.4 micron band.

As can be seen from Figures 1 and 3, even the hydrocarbon absorption bands which are most sensitive to pressure-broadening are not significantly affected by appreciable variations in pressure in the range near 760 mm. Variations in atmospheric pressure by 20 or 30 mm from the pressure used in the calibration analyses should have no significant effect on the accuracy of the determination.

TABLE II. COMPARISON OF PRESSURE-BROADENING EFFECTS OF ONE ATMOSPHERE OF AIR AND $CO_2$ ON ETHYLENE, ACETYLENE AND PROPYLENE

| *Compound* | *λ, μ* | *Partial pressure, mm* | *Broadening Gas* | *Absorbance*[a] |
|---|---|---|---|---|
| Ethylene | 10.52 | 0.63 | air | 0.506 ± 0.024 |
| | | | $CO_2$ | 0.518 ± 0.043 |
| | | 1.03 | air | 0.856 ± 0.028 |
| | | | $CO_2$ | 0.907 ± 0.019 |
| Acetylene | 7.63 | 5.0 | air | 0.222 ± 0.003 |
| | | | $CO_2$ | 0.257 ± 0.005 |
| Acetylene | 7.63 | 10.0 | air | 0.361 ± 0.001 |
| | | | $CO_2$ | 0.432 ± 0.003 |
| Propylene | 10.95 | 0.97 | air | 0.472 ± 0.006 |
| | | | $CO_2$ | 0.484 ± 0.002 |
| *trans*-2-Butene | 10.37 | 1.92 | air | 0.718 ± 0.012 |
| | | | $CO_2$ | 0.733 ± 0.010 |

[a] Average values and std. dev. of 5—15 experimental determinations

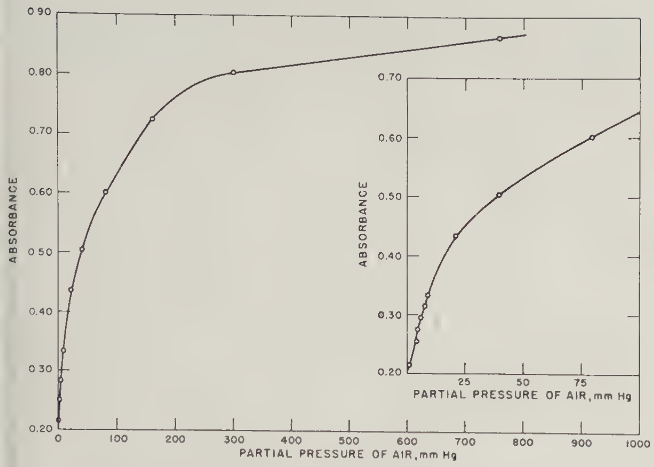

Fig. 1. Pressure-Broadening of 10.5 Micron Band of Ethylene (1.15 mm Ethylene) by Air

### Discussion

The present results provide additional evidence as to the appreciable pressure-broadening experienced by at least some of the prominent infrared absorption bands of two- and three-carbon hydrocarbon molecules. The data presented in the present work indicate that the bending vibrations of 1-butene and trans-2-butene are only slightly pressure-broadened. No pressure-broadening has been reported previously for the 8.47-micron band of isobutene or the 6.26-micron band of 1,3-butadiene (*2*). However, these investigators (*2*) did find slight pressure-broadening of the 11.0 micron band of 1,3-butadiene.

Pressure-broadening has been reported previously for one of the components of the 14.8-micron band of benzene (*6*). The data given in Table I for benzene clearly indicate that the 9.50-micron band also undergoes pressure-broadening. While deviations from ideal gas behavior in the gas mixture compared to the benzene alone would have a slight effect in the same direction, the magnitude of such an effect would be too small. No artifact occurs to the present investigators which would explain the results. Consequently, at present, we must accept the results available as providing evidence for a real pressure-broadening effect for as large a molecule as benzene.

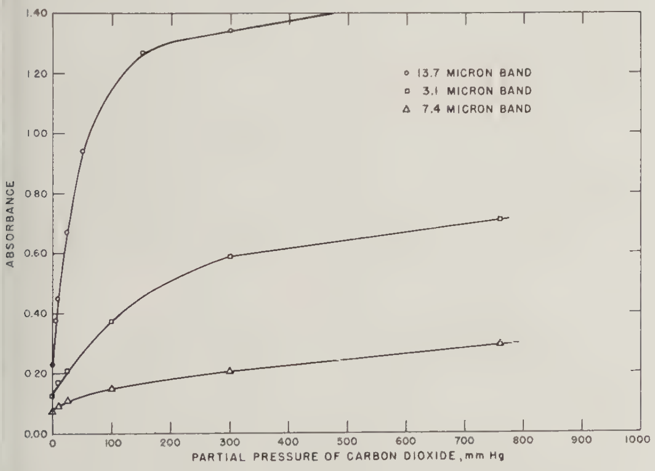

Fig. 2. Pressure-Broadening of Several Acetylene Bands (0.7 mm Acetylene) by Carbon Dioxide

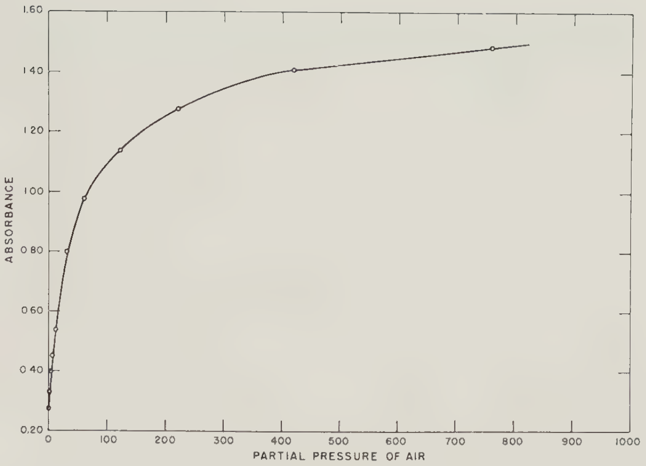

Fig. 3. Pressure-Broadening of 13.7 Micron Band of Acetylene (0.84 mm Acetylene) by Air

The results obtained for the 3.1-, 7.4-, and 13.7-micron bands of acetylene indicates the wide variations in pressure-broadening existing among different bands of the same molecule. Caution should be used in drawing conclusions about the effects of pressure-broadening on other infrared bands of a molecule from experimental results on any given band of that molecule.

The present investigation does indicate that $CO_2$ often has a greater pressure-broadening effect on the bands of light hydrocarbon than does air. However, the difference is not enough to make 10 or 15% of $CO_2$ in a combustion mixture of significance in comparison with an equivalent amount of oxygen. Consequently, calibration mixtures of hydrocarbons made up in air should be adequate in reproducing conditions in combustion mixtures for the purposes of infrared analysis.

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# The Spectrochemical Analysis of Magnesium and Its Alloys for Beryllium, Lead, and Other Trace Elements by Solution And Salt-Cap Techniques

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### Abstract

Spectrographic solution and salt-cap techniques are described for the determination of beryllium, lead, and other trace elements in magnesium alloys in the range 0.0001-0.3%. Beryllium is determined with a precision within ±4% between 0.0001 and 0.01% with a high voltage spark source and a rotating disk electrode method. Comparative sensitivity and precision results are given for Al, Ca, Cu, Fe, Mn, Pb, Ni, Sn, and Zn with a high voltage spark condition using the rotating disk electrode and an ac arc salt-cap technique. Considerable improvement in sensitivity for Al, Ca, and Pb is demonstrated with use of an argon atmosphere in the ac arc work.

Beryllium, lead, and other trace elements must often be determined in magnesium alloys for quality control purposes by chemical, spectrographic, or direct techniques. For any such instrumental calibration independent analyses are required to provide alloy compositions of known concentrations as standards.

The present work describes spectrographic solution and salt-cap techniques employed in analyzing for some commonly encountered elements. Beryllium was determined by use of a solution-spark-rotating disk electrode technique. This method was also applied to the determination of other elements such as copper, manganese, iron, and nickel. Beryllium is important in magnesium alloys because of its ignition prevention properties when present in 0.0001-0.02% concentrations. A sensitive and precise method for its determination is thus necessary.

A salt-cap ac arc technique is also described as used when better sensitivity was required and applied especially to Pb determinations.

### Rotating Disk Electrode Method

In recent years the rotating disk electrode technique for spectrographic solution analysis has been developed and applied to a variety of problems. Since its proposed use *(1)* as a method of introducing a liquid sample into the excitation zone, several applications in the oil and steel industries have been reported. Applied Research Laboratories *(2)*, Pagliassotti and Porsche *(3, 4)*, Key and Hoggan *(5)* have reported extensive work in determining various metallic impurities in lubricating oils and additives. Other work by the same authors *(6, 7)* has utilized the technique in the analysis of silica-alumina, cracking catalysts.

Further application of this technique in the steel industry has likewise been reported by several authors *(8-10)* for the analysis of common constituents in steel. Rust and Edgar *(11)* have included analysis for cerium in ferrous materials. An ASTM suggested method for the analysis of titanium metal and sponge is also available. *(12)*.

In a comparative study of different spectrographic techniques by Baer and Hodge *(13)*, the rotating disk electrode method was described as possessing good sensitivity and reproducibility in a high voltage spark discharge. In this laboratory HCl, $HNO_3$, $H_2SO_4$ solutions, and kerosene have been analyzed with good precision and adequate sensitivity to recommend its use for many problems.

The general description of a rotating disk electrode assembly and its attendant techniques has previously been given *(8)*. To enable use of concentrated acids whose vapors would be corrosive to the source housing and electrical circuitry, the assembly design was modified by the addition of a vented polystyrene discharge chamber with appropriate holes for the optical path and counter electrode. A sliding door was provided for introducing the solution-containing porcelain combustion boats.

### Equipment and Spectrographic Conditions

Excitation was obtained by the use of a high voltage, air-interrupted spark discharge *(14)* with the electrical parameters and other spectrographic details for beryllium analysis described in Table I as condition A. The spectrograph used in all work reported in this paper was a Baird-Atomic 3-meter grating instrument with photographic recording, having a reciprocal dispersion of 5.5A/mm in the first order. Eastman Kodak Spectrum Analysis No. 2 plates were used to record the spectra.

United Carbon Products No. 106 disks and No. 100U counter electrodes were used with Coors No. 1 porcelain combustion boats. UCP No. 2025 mandrels were first used and later replaced by a tantalum mandrel. The mandrel was rotated at 10 rpm. A prespark period of 7-8 sec on the dry disk was found desirable to increase disk porosity and hence improve pickup of the solution.

### General Procedure

Standard solutions were prepared containing 5% of the metal or alloy to be analyzed. Hydrochloric acid was used in preparation of standard beryllium solutions. After dissolution of 5 g of the alloy composition in 60 ml of acid, desired standard concentrations were prepared by the addition of known amounts of impurities to aliquots and making to 10 ml final volumes. Samples received similar dissolution treatment in preparation for spectrographic analysis as 5% solutions.

### Beryllium Analysis

Typical magnesium alloys analyzed contained 3, 6, or 9% Al plus 1-2% Zn(AZ type), 6% Zn and 0.7% Zr (ZK 60), and 1% Zn with traces of rare earth elements (ZE 10). $BeSO_4 \cdot 4H_2O$ (Fisher c.p.) was used as

Table I. Excitation and Exposure Conditions

| | *Condition A* | *Condition B* |
|---|---|---|
| Discharge voltage, v | ~10,000 | ~25,000 |
| Capacitance, $\mu f$ | 0.007 | 0.002 |
| Inductance, $\mu h$ | 10 | 260 |
| Discharges/cycle | 10 | 10 |
| Radio-frequency current, amp | 11 | 6.4 |
| Spectral region, A | 2300-3700 | 2300-5100 |
| Slit width, mm | 0.050 | 0.050 |
| Spark preburn period, sec | 8 | 8 |
| Spark exposure period, sec | 20 | 40 |
| Intensity reduction | 32% transmission screen | none |

beryllium base material and standards were prepared from 0.0001-0.03% Be based on the alloy weight in solution.

Analytical curves were prepared by plotting concentrations vs. intensity ratios for the line pairs Be 3130.42/Mg 3073.99 and Be 3131.07/Mg 3073.99 from 0.0001-0.01 and 0.0001-0.03% Be, respectively. The more sensitive 3130.42 A line was useful especially below 0.001% Be while the 3131.07 A line covered higher concentrations more satisfactorily.

Alloys containing from 3-9% Al gave one curve. Pure Mg, ZE 10, and ZK 60 alloys yielded a curve with increasing displacement from the above one at concentrations greater than about 0.0004% Be (Figure 1). Coefficients of variation obtained at the 0.001, 0.005, and 0.01% levels from duplicate runs on 4 or 5 plates were 3.6, 4.9, and 3.8%, respectively.

Possible interference from Zr 3131.11 on the Be 3131.07 line suggested in the M.I.T. tables *(16)* was checked and found absent at the 0.7% Zr level present in ZK60 alloys. A maximum of about 0.002% Be was detected in such Zr-containing alloys. Beryllium above this level was apparently precipitated by Zr in the alloy melt.

The condition B source described in Table I, which was found desirable for excitation of most elements, was not satisfactory for low beryllium because of partial obscuring of the 3130.416 A line by a couplet of unidentified lines apparently originating from water excitation.

### Other Impurities in Magnesium by the Rotating Disk Electrode

The rotating disk electrode method was extended to include the determination of other impurities such as Cu, Fe, Mn, Ni, Pb, and Sn often found in less than 0.01% concentration in magnesium metal or alloys. In a search for suitable source conditions, various parameters were investigated. Capacitance was varied from 0.002-0.007μf and inductance from 10-513μh. Final discharge parameters were selected to avoid objectionable boiling of the solution and excessive graphite consumption noted under certain high energy discharge conditions. The high inductance, high voltage, Condition B source described in Table I which favored the excitation of arc lines was found suitable for the determination of these elements.

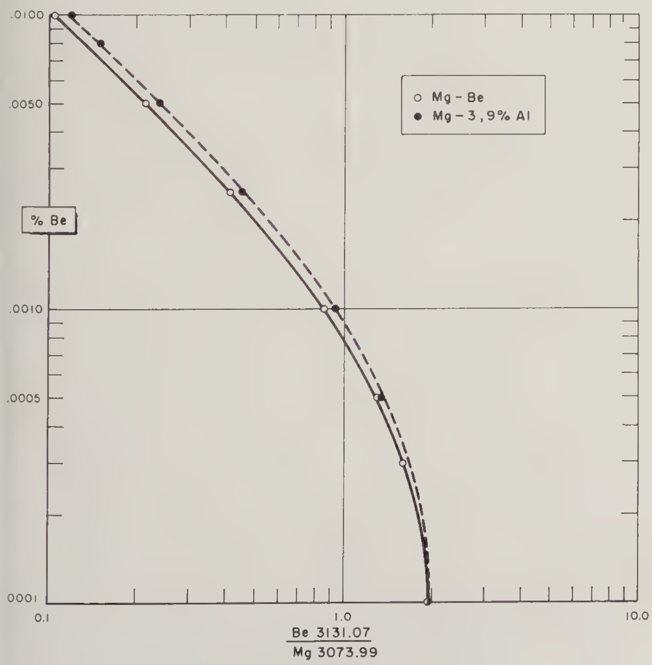

FIG. 1. Be ANALYTICAL CURVES

TABLE II. SENSITIVITIES AND PRECISION WITH THE CONDITION B SOURCE[a]

| *Analytical line* | *Concentration Range, %* | *Coefficient of Variation (0.01% level)* |
|---|---|---|
| Al 3082.15[b] | 0.005-0.3 | 14.5 |
| Ca 3179.33 | 0.003-0.3 | 5.9 |
| Cu 3273.96 | 0.0001-0.03 | 5.0 |
| Fe 3020.64 | 0.003-0.3 | 11.4 |
| Mn 2593.73 | 0.0001-0.01 | 4.1 |
| Pb 2833.07 | 0.03-0.3 | N.D. |
| Ni 3414.76 | 0.001-0.3 | 4.3 |
| Si 2881.58[b] | 0.005-0.3 | 9.5 |
| Sn 3034.12[b] | 0.005-0.3 | 10.9 |
| Zn 3345.02 | 0.03-0.3 | N.D. |

[a] Reference line, Mg 3073.98
N.D.—Not detectable
[b] Background substracted.

Standards were prepared as the nitrate and contained up to 0.3% impurities based on the metal weight. The described Condition B source (Table I) was used, and analytical curves were prepared conventionally. Analytical lines used, useful concentration ranges, and precision obtained are given in Table II with spectral background intensity subtracted as indicated. The practical detection limit was determined as the concentration limit at which the difference between spectral line and adjacent background transmission was less than about 3 cm on a 0-100 cm transmission microphotometer scale. Precision was poorer as the line intensity approached background intensity and was best for Cu, Mn, and Ni whose line densities at the 0.01% level were considerably above background levels.

Prepared standards containing the impurity elements only down to 0.0001% concentration in 10% by volume HCl solutions were run using the Condition B source and a 30 sec exposure. Sensitivities of the elements in μg/ml solution are given in Table III and compared with sensitivities calculated from Table II data in the magnesium matrix. Some suppression of Al, Pb, and Zn by Mg is indicated while Cu, Mn, and Fe are enhanced.

### AC Arc Salt-Cap Method

An ac arc salt-cap procedure using a source similar to that described by Owens *(15)* was employed when lower detection limits were desired for Ni, Pb, and Sn. Nitric acid was used instead of HCl in the preparation of standards and samples to avoid precipitation of lead when present in high concentrations. Molybdenum was added as an internal standard at a concentration of 1.0 mg (1.0 ml of a 0.1% solution) per 100 ml of the 5% alloy solution. Thirty μl of the 5% solution as the nitrate were placed on each of a pair of kerosene-impregnated graphite

TABLE III. SENSITIVITIES IN DILUTE ACID AND MAGNESIUM SOLUTIONS[a]

| | *10% HCl* | *5% Mg Solution* |
|---|---|---|
| Al | 1 | 2.5 |
| Ca | 1 | 1.5 |
| Cu | 1 | 0.05 |
| Mn | 1 | 0.05 |
| Ni | 1 | 0.5 |
| Fe | 5 | 1.5 |
| Pb | 5 | 15. |
| Sn | 5 | 2.5 |
| Zn | 5 | 15. |

[a] Condition B Source

TABLE IV. EXCITATION AND EXPOSURE CONDITIONS WITH THE AC ARC

| | |
|---|---|
| Primary voltage, v | 2400 |
| Ac current, amp | 4.4 |
| Spectral region, A. | 2300-5100 |
| Slit width, μ | 50 |
| Prearc time, sec | 10 |
| Exposure time, sec | 45 |

electrodes, ¼ in. diam. and ¾ in. long. Loaded electrodes were dried over gas microburners and stored for one hr in an oven at 100°C before running. Other spectrographic details are given in Table IV. Table V lists analytical line pairs, useful concentration ranges, and precision coefficients obtained at the 0.01% level.

In order to improve sensitivity for Al and Ca whose sensitive arc lines occur in regions normally obscured by cyanogen bands, an argon atmosphere was investigated. Background and cyanogen structure were effectively reduced with this atmosphere and thus sensitivity for Al and Ca was improved to 0.001 and 0.0005%, respectively, using the 3961.53 and 3968.47 A lines. Lead, 4057.82 A, also became usable and sensitive to 0.0005%. Five to about twenty fold gains in sensitivity for Al, Ca, Pb, and Zn are thus noted in Table V over values given by excitation in air using other analytical lines.

Similarly, a hundredfold gain in detection of Zn to 0.0005% was achieved by use of an ultraviolet sensitive Ilford Q2 plate to record the Zn 2138.56 line. Considerable care must be observed in handling these plates to avoid scratching or marring.

Lead determinations were made in Mg, Mg-3% Al, and Mg-6% Al-3% Zn (AZ 63 type) alloys with the ac arc technique to provide desired sensitivity. Standard 5% solutions of the alloy compositions were prepared to check matrix effects and electrodes were prepared as described. Parallel shifting of the analytical curve prepared for pure Mg was caused by the addition of 3-6% Al and also by the AZ63 alloy composition. Spectral background intensity was subtracted from the Pb line to provide more desirable curve slopes (Figure 2).

## Discussion

The combined methods as outlined provide for the analysis of magnesium and its alloys for common impurity elements. Elements other than those listed could be readily determined by the described techniques by incorporation in the standards and by use of appropriate spectral ranges and photographic emulsions. Na, K, and Li can thus be determined using a I-N plate while Zn sensitivity was improved using an ultra-violet sensitive plate to record the 2138.56 line. Higher concentrations of impurities can be satisfactorily determined by either method with suitable dilutions or by extending the range of the standards.

TABLE V. SENSITIVITY AND PRECISION WITH THE AC ARC[a]

| *Element* | *Concentration Range, %* | *No. Determinations* | *Coefficient of Variation (0.01% level)* |
|---|---|---|---|
| Al 3082.15 | 0.03-0.3 | — | N.D. |
| Al 3961.53 (Zr absent)[bc] | 0.001-0.1 | 6 | 14.9 |
| Ca 3179.33 | 0.005-0.3 | 6 | 26.4 |
| Ca 3968.47[c] | 0.0005-0.01 | 6 | 10.9 |
| Cu 3273.96 | 0.0001-0.03 | 15 | 9.3 |
| Fe 3020.64 | 0.0005-0.1 | 15 | 8.4 |
| Mn 2593.73 | 0.0001-0.05 | 6 | 10.4 |
| Ni 3414.76 | 0.0005-0.05 | 15 | 9.2 |
| Pb 2833.07[b] | 0.003-0.2 | 15 | 8.3 |
| Pb 3683.47[c] | 0.0005-0.1 | 6 | 11.9 |
| Sn 3175.02 | 0.0005-0.1 | 15 | 5.5 |
| Zn 3282.33 | 0.05-0.3 | — | N.D. |
| Zn 3345.02[c] | 0.003-0.2 | 6 | 13.2 |

[a] Reference line, Mo 3208.83
N.D.—Not detectable.
[b] Background subtracted.
[c] Argon atmosphere

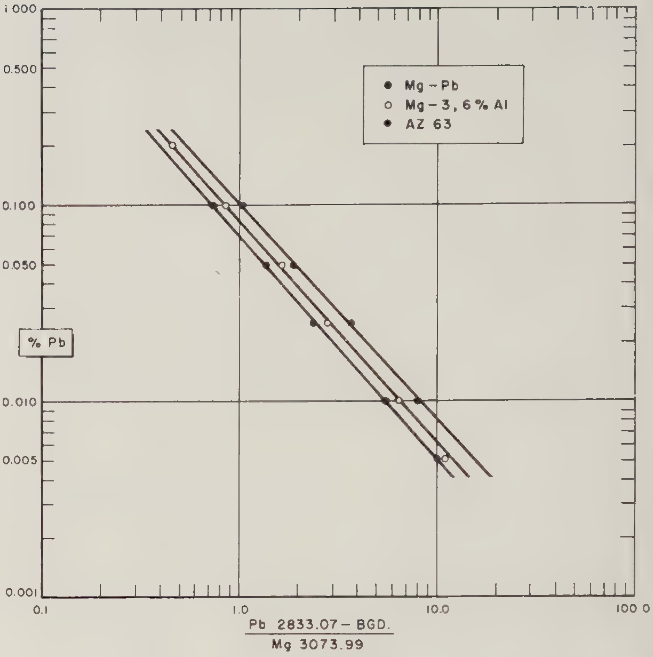

FIG. 2. Pb ANALYTICAL CURVES

The ac arc technique is generally capable of better sensitivity in this matrix than the rotating disk electrode under the conditions employed. Earlier work with this technique has however demonstrated considerable analytical curve shifting with such hygroscopic compounds unless careful control and consistency in time of drying and storing of electrodes is exercised.

The rotating disk electrode has demonstrated improved precision with some elements over the salt-cap technique plus time economy in sample handling. Hydration problems associated with deliquescent Mg and Zn salts are reduced. Such advantages coupled with its directness recommend it as a method for determining higher concentration impurities generally. It is also quite applicable to trace work in many specific cases.

## Acknowledgement

The many helpful suggestions obtained from T. M. Hess in the preparation of this manuscript are gratefully acknowledged.

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# Soviet Spectrographic Equipment

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## Abstract

Standard Soviet spectrographic equipment is reviewed, and some of the properties of the newer Soviet spectrographic equipment are briefly discussed.

Owing to a centrally administered production, there is a relatively small variety of standard spectroscopic instruments in the U.S.S.R.* However, the standard equipment must not be confused with the apparatus recently developed. The Soviet research in this field is carried out on an immense scale, and the author may claim that no spectroscopic instruments exist that could not be labeled "Made in U.S.S.R.".

## Standard Prism Spectrographs

ISP-28 and its older version, ISP-22, are typical Cornu quartz instruments comparable, e.g., to the Hilger E 498 (*1-3*). A spherical mirror is employed instead of the usual collimator lens (Figure 1). The photographic plate need not be curved to follow the focal surface of the camera lens. However, the plate tilt of this instrument is 42° at 2600 A. Also, the spectral lines are but slightly curved because of relatively great focal lengths of the camera lens and the collimating mirror (830 and 700 mm respectively). The high spectrum quality is achieved at the expense of some speed. The instrument is equipped—as is most apparatus to be discussed—with a three-lens system of slit illumination. In the Russian instruments, the first two (spherical) lenses of the three-lens system of illumination are achromatically corrected so that the analytical gap may be easily controlled at the intermediate image diaphragm. In the ISP-22, the quartz prism and quartz camera lens might be replaced by a glass Rutheford prism and a glass lens, i.e., this standard instrument could be used for work in the wavelength range over 3500 A with somewhat more convenient dispersion (Table I). As in Central Europe, the popularity of medium dispersion spectrographs is very high in the U.S.S.R., and the ISP-22 has probably been the most widely used in Soviet spectrographic laboratories. The optical system of the newer ISP-28 is essentially the same (Figure 1), but the ISP-28 is built to provide much greater ease of handling. Only the ISP-28 version is produced commercially at present (*4*).

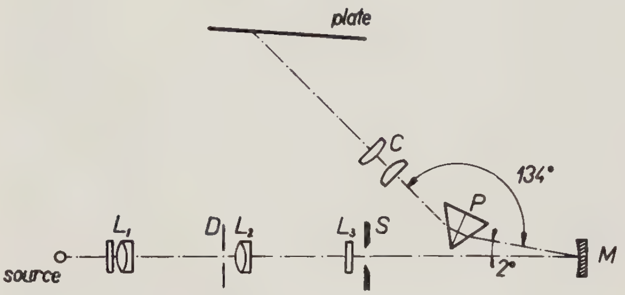

FIG. 1. SCHEMATIC DIAGRAM OF THE MEDIUM DISPERSION ISP-28

$L_1$, $L_2$, $L_3$—Lenses of the three-lens system of slit illumination, D—Diaphragm of the three-lens system of slit illumination, M—Collimating mirror, C—Camera-lens, S—Slit.

KSA-1 and its older version, KS-55, are the usual Littrow instruments comparable, e.g., to the Hilger E 492 (*1*) (Figure 2). In order to overcome an inherent defect in most Littrow spectrographs—the reflection of light from the spherical lens to the plate—a concavo-convex lens is used instead of the usual plano-convex condenser. The first surface of the lens is curved so that the reflection from it is screened by the camera case while the reflection from the second surface is blocked out by means of a "point" screen. This is achieved at the expense of the quality of the slit images; however, the somewhat

TABLE I. RECIPROCAL LINEAR DISPERSION OF THE ISP-28 AND THE KSA-1

| *Wave-length, A* | *Dispersion, A/mm* | | | |
|---|---|---|---|---|
| | *ISP* | | *KSA* | |
| | *Quartz* | *Glass*[a] | *Quartz* | *Glass* |
| 2000 | 3.5 | | 1.2 | |
| 2500 | 9.0 | | 2.5 | |
| 3000 | | | 4.6 | |
| 3100 | 16.0 | | | |
| 3500 | | | 7.2 | 3.4 |
| 3600 | 25.0 | | | |
| 4000 | 39.0 | 10 | 11.5 | 5.5 |
| 5000 | | | 21.0 | 11.6 |
| 6000 | 110.0 | | 34.0 | 21.3 |
| 7000 | | | | 33.0 |
| 8000 | | | | 46.0 |

[a] No longer used in the ISP-28.

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*Each type of instrument has its representative with no more than two or three different models.

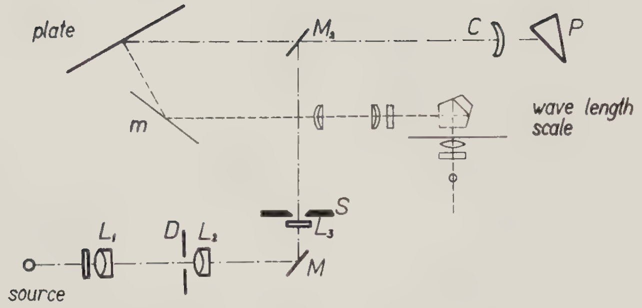

FIG. 2. SCHEMATIC DIAGRAM OF THE AUTOCOLLIMATING KSA-1

L, D—See Fig. 1, S—Slit, M, $M_2$—Plane mirrors, C—Collimator-camera lens, m—Plane mirror of the wavelength projection system.

less perfect image as formed by the concavo-convex lens is said (*1*) not to be critical. The instrument is equipped with an interchangeable glass prism and glass collimating-camera lens. Three wavelength-selecting adjustments are combined in one operation for either quartz or glass optics; however, the glass prism and lens must be changed for the quartz optics by hand. In place of the usual total-reflecting prism, a plane (aluminum first surface) mirror is used to refract the light path within the light-tight spectrograph case. The wavelength range of 2000-8000 A can be photographed on three lengths of the 24 cm plate (quartz prism and lens), and the range from 3600 A to 8000 A covers two lengths of the plate (glass optics). There are no essential differences in the dispersion of the KSA-1 and the Hilger E 492 (Table I) with the focal length of the collimator-camera lens of the KSA-1 equal to 1896.5 mm (quartz) and 1684.5 mm (glass) at 5893 A.

There are two standard glass prism instruments. The older ISP-51 (*1*) is a three prism glass spectrograph. The Fösterling prism train enables attainment of a linear reciprocal dispersion of 24.5 A/mm at 3600 A with a camera of 120 mm focal length, or 11 A/mm with a 270 mm camera. Neither the two remaining cameras built as special units, namely, the UF-84 and UF-85 (*4*) differ in their focal lengths from those of the Zeiss (Jena) three-prism glass spectrograph. With the UF-85 autocollimation camera, a reciprocal linear dispersion of 2 A/mm at 4000 A is attained (*2,5*). The second three-prism instrument manufactured commercially (*4*) is the ISP-67 (*6*). A collimating lens of focal length of 1000 mm is employed, and the instrument is equipped with four interchangeable cameras whose focal lengths are 180, 500, 1500, and 3000 mm resp. With the latter, reciprocal linear dispersion of 0.77 A/mm at 4005 A is attainable, and the resolving power amounts to 260,000 (*4*).

### Other Prism Instruments

Besides the standard instruments mentioned, a vacuum fluorite spectrograph has been developed (*7,8*) suitable for work in the far ultraviolet region. The surfaces of the simple (achromatically uncorrected) lenses are curved parabolically so that high spectrum quality is achieved.

Large aperture instruments have also been designed (*8*) such as the ISP-66, whose linear aperture is 4.6. As in the ISP-28, a collimating mirror is employed. It is curved parabolically to attain high spectrum quality with a collimating mirror of such a short focal length. Still more effective is the ISP-26 (*8*) whose linear aperture is 0.7.

Besides the instruments mentioned, many other prism instruments have been developed in the U.S.S.R., and the interested reader should consult the original papers (*8,9,13*). However, these apparatus are not considered "standard equipment".

### Steeloscopes

In Soviet Russia, a relatively great variety of steeloscopes exists. Only few of them will be mentioned in the present paper. The three-prism Steelometer ST-7 (*10*) is equipped with a wedge photometer, permitting a quantitative estimation of metal percentages. The Steeloscope SL-11 employs two dispersing prisms (*11-13*) and uses the autocollimating principle with a light source built into this spectroscope (*4*). The Steeloscope SLP-2 is a portable field spectroscope; it is produced on the commercial scale as well (*4*). More information on similar instruments may be found in a short book (*13*).

### Gratings

Great advances have been made in this field during the past ten years. Gratings are claimed to have been ruled in the Soviet Union that seem to meet the highest requirements. The standard 600 and 1200 rulings/mm gratings are said (*14*) to show no Lyman ghosts, and the Rowland ghosts' intensity is as small as 0.02% of the parent line intensity in the best 600 rulings/mm gratings. Gratings are obtainable blazed for a wide range (*14*); gratings with 1200 lines/mm do not show any essential weakening of the light extent at 1976 A when blazed for the 1st order 2800 A (*15*). Maximum light amounts to 80% (600 rulings/mm) and 70% (1200 rulings/mm) (Table II). Resolving power equal to 400,000 is said to have been attained when higher spectrum orders are employed (*14*). Information on replica gratings have been published (*16*).

Concave gratings are offered having the standard 600 and 1200 rulings/mm with the radius of curvature of 1000, 1995, 2992, and 6020 mm (aluminum-on-glass surface) and ruled areas up to 145 x 70 mm.

TABLE II. COEFFICIENT OF REFLECTION OF THE SOVIET DIFFRACTING GRATINGS (*14*)

| *No. of lines/mm* | *Spectrum order* | *Coefficient of reflection, %* | |
|---|---|---|---|
| | | *mean value* | *maximum value* |
| 600 | 1st | 70 | 80 |
| 600 | 2nd | 55 | 65 |
| 600 | 3rd | 45 | 55 |
| 1200 | 1st | 50 | 70 |

### Grating Instruments

DFS-2 is a 2 meter concave grating spectrograph employing the Paschen-Runge mounting (*8,15*). It is the first Russian instrument employing a concave grating. Two gratings are built in the instrument one above the other; the lower grating is one with the standard 600 lines/mm, and the standard 1200 grooves/mm are engraved on the upper grating. Each of the aluminum-on-glass gratings has its own slit and camera so that two spectrographs are provided in a single housing. The whole spectrum (2000-10000 A) covers the lengths of 1 or 2 meters according to which grating is used. The linear reciprocal dispersion attained is 8.3 A/mm (600 lines/mm grating) and 4.2 A/mm with 1200 lines/mm. The resolving power of this latter grating is 84,000. Step filters are set immediately in front of the emulsion because of the astigmatism of the mounting. The spectrograph is equipped with a camera enabling it to photograph as much as 0.5 meter spectrum length at one setting. The linear aperture of the DFS-2 is 30. The instrument has never been manufactured on the commercial scale and photographic picture of it may be found in (*8*).

DFS-3 (*8*) is a large Ebert stigmatic spectrograph. Interchangeable plane gratings (600, 1200 rulings/mm) are employed in connection with a concave mirror whose focal length is 4 meters. The 24 cm plate covers the range of some 500 or 1000 A according to the grating used. Consequently, the grating must be turned correspondingly around its vertical axis at each wavelength selection. The plate factor is 2 A/mm (1200 lines/mm grating), the resolving power is 144,000, and the linear aperture is 42. Hyperfine structure of the mercury lines may be seen on the plate when higher orders employed (For the reproduction of the spectrogram, see *(14)*.)

DFS-4 (*8*) is built as a large aperture instrument (linear aperture of 7.3) using a collimating-camera lens of the focal length of 1200 mm. Two interchangeable (the standard numbers of lines/mm) plane gratings blazed for the visible spectrum range are employed (dimensions 150 x 150 mm) and reciprocal dispersions of 13.5 and 6.5 A/mm are obtainable. The spectra can be photographed, or alternatively, the instrument may be used in connection with the photomultiplier FEU-17 (see **Direct Reading Instruments**). Entrance and exit slits are as high as 40 mm.

DFS-5 (*9*) is a large vacuum spectrograph designed for work in the range of 500-2000 A. A 1200 lines/mm concave grating is employed whose radius of curvature is 3 meters, and it has a Paschen-Runge mounting.

DFS-6 is a grazing incidence ($i=82^\circ$) vacuum spectrograph (1 meter concave grating, 600 lines/mm ruled on glass) (*8*). It is designed for work in the range 60-2000 A in the first order. Its linear reciprocal dispersion is 3 A/mm (60 A) and 8 A/mm (2000 A). Unlike the previous instruments, it is manufactured on the commercial scale (*4*).

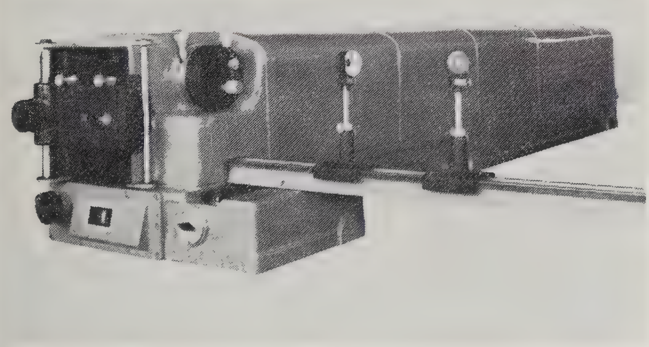

Fig. 3. The Plane Grating DFS-8 *(Courtesy of The Commission for Spectroscopy of the Academy of Sciences of the U.S.S.R.)*

The next instrument to be discussed, the DFS-8 (Fig. 3) (*9*), is also produced commercially (*4*). In the commercial version, it employs a 100 x 45 mm plane grating with 1200 rulings/mm. The spectrum range from 2000 to 10000 A is 2.7 meter long, but only 540 A may be photographed on a 13 x 18 cm plate at one setting, i.e., at one tilt of the grating around its vertical axis. The autocollimating principle is employed, and the focal length of the collimator-camera mirror is 2648.5 mm. The linear reciprocal dispersion is 3 A/mm with the linear aperture of 35.

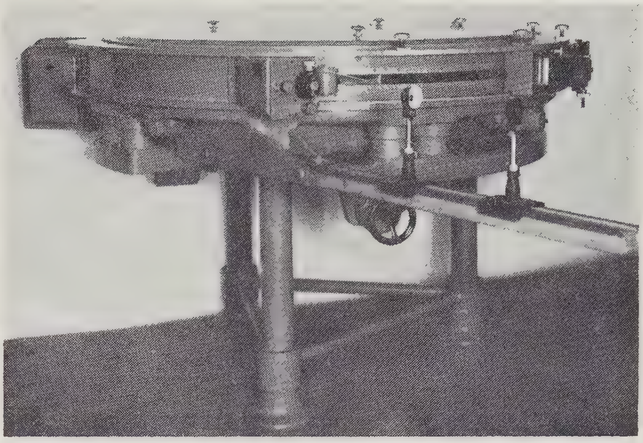

Fig. 4. The Paschen-Runge DFS-9 *(Courtesy of The Commission for Spectroscopy of the Academy of Sciences of the U.S.S.R.)*

The 2 meter DFS-9 (Fig. 4) built-in Paschen-Runge mounting (*4*) is also produced commercially. With the standard 1200 lines/mm grating, it performs as a commercial version of the upper part of the DFS-2 with a dispersion of 4.2 A/mm in the 1st spectrum order, the theoretical resolving power of 84,000, and the linear aperture of 30 (the ruled surface being 70 x 50 mm). As much as 0.5 meter spectrum length may be photographed on the usual moving-picture film; smaller parts of the spectrum may be taken with a small camera. The angle of incidence is approximately 41°, and the angles of diffraction are $-24.5^\circ$ for 2000 A and 33° for 10,000 A. Intensity-modifying devices are set in front of the emulsion as was the case in the DFS-2 that evidently served as a prototype.

Similarly, the DFS-13 is a commercial version of the DFS-3.

The SP-48 is a plane replica grating (1200 rulings/mm) instrument whose linear aperture is 0.8 and linear reciprocal dispersion is 100 A/mm. It is designed for work in the range 3800 - 8000 A and is available commercially.

### Direct Reading Instruments

Several direct reading instruments have been designed. The first to be mentioned in the present paper is the Photoelectric Steelometer FES-1 (*9,17*). The instrument consists of a three-prism glass spectrograph, an ac source with an electronic control (see, **Excitation Sources**) in connection with two standard antimony-cesium photocells (noise current of the order $10^{-15}$ amp). One of the cells registers the light reflected from the first surface of the prism, and the second registers the spectral energy of the line of the element to be determined. The photocurrent charges the condensers. The charges of the condenser are measured by means of an electrometer with a dynamic condenser (*18*) and recorded by means of the potentiometer EPV-01. Analytical pair intensity ratios are given and the undispersed light acts as the internal standard. Working entirely automatically, it is produced on the commercial scale.

The Photoelectric Spectrometer DFS-10(g) employs a 2 meter Paschen-Runge grating spectrograph (1200 lines/mm, Rowland circle in vertical position) with 36 exit slits placed along the Rowland circle. Monochromatic light impinges on the standard SCV-9 photocells working in the range from 2200 to 5500 A (no photomultipliers are used). Eleven + 1 lines are registered simultaneously, and 12 analytical programs are possible. The registering device employes a logarithmic impulse voltmeter connected with each of the eleven condensers one after another with the result being registered by means of the electronic electrometer EPP-09 (For details on the electrical circuit, see (*19*)). It may be worth mentioning that the slit illumination is made by means of a Rasterkondensor. The instrument is built in order to be independent of temperature changes.

The large aperture DFS-12 is a plane grating instrument (plane grating 150 x 140 mm, 600 lines/mm) designed for work in the 2nd order, 3600 - 6500 A. Either single or double monochromatization may be used. The photomultiplier FEU-17 with dc amplification serves as the registering device, and instantaneous intensities are recorded (*9*).

The direct-reading attachment FEP-1 is manufactured for the ISP-51 (*4*). It is designed for work with weak light sources. It consists of an exit collimator (focal length of 300 mm) and of amplifying and registering devices, i.e., the photomultiplier FEU-17 and the recorder EPP-09.

Many other apparatus of similar type have been developed such as the SP-61 for work with light sources of very short duration, or the SP-64, another high-speed recording instrument (*8*). It is beyond the scope of the present paper to describe them all, and the interested reader should consult the original papers (*13*).

### Microphotometers

The non-recording MF-2, similar in design and function to the Zeiss (Jena) Schnellfotometer (*1*), and the self-recording MF-4 are used (*8*) and manufactured commercially (*4*). The optical scheme of the MF-4 is essentially that of the MF-2, but the former may be used either as a non-recording or a self-recording instrument (*20*) using selenium photocells.

### Accessories

Rotating sectors are rarely used, but platinum and similar step filters are manufactured instead of sectors. As a rule, 3 or 8 step filters are employed with the latter having proved to be useful in the *Method of Photometric Interpolation* (*21*), which is very popular in the U.S.S.R.

Vertical projectors, PS-18 and DSP-1, are furnished with the standard spectrographs. The former is a simple lantern projector, and the latter is a device enabling comparing sample and master spectra (*1*). Both are vertical projectors using a horizontal projection screen. More recently, a special projector with a vertical projection screen has been designed in which the optical system suppresses the effects of the emulsion graininess (*8*).

### Excitation Sources

No special dc arc unit has been produced on a large scale, although one type of an original dc arc with an impulse discharge has been suggested (*22*).

The standard ac unit is the DG-2 (*4*), which is a version of the older DG-1 (*1*), and both are based on a circuit described earlier (*23-25*). It consists of a high frequency circuit in addition to a normal (50 cycles in Europe) circuit with an adjustable output (Figure 5A). The unit can serve as a low voltage spark as well (Figure 5B). The high frequency igniting the 220 v arcs can be taken out independently, so that 3 different sources are combined in this relatively simple and inexpensive unit.

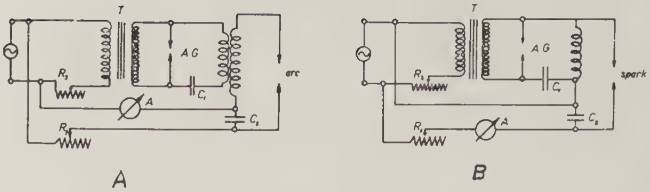

Fig. 5. Simple Circuit Diagram of the DG Arc (A) and Spark (B)

$R_1$—Resistance of the 50 cycle circuit, $R_2$—Resistance of the high frequency circuit, $C_1$—Condenser of the high frequency circuit, $C_2$—Condenser of the 50 cycle circuit, A. G.—Auxiliary gap, T—Transformer of the high frequency circuit.

The design of spark sources, the older IG-2, and the standard IG-3 that is produced at present (*4*) is also due to an older circuit (*26,27*). The analytical gap is coupled in shunt with a coil choke passing the low frequencies only. When putting charge on the condenser C (Figure 6), no potential drop occurs at the analytical gap, but the potential drop at the auxiliary gap grows until a high frequency discharge occurs at the analytical gap since it is blocked by the choke, R.

Recently, an ac source with an electronic control has been designed (*28*), and is available as the GEU-1 (*4*). The source can work as a low voltage arc and spark, or the current may be rectified by means of the electronically timed ignition of the arc. The unit is considered useful in connection with the direct reading instruments.

A great many other light sources have been designed for special tasks of the spectrographic analysis as described in (*29-32*), but they are not manufactured commercially.

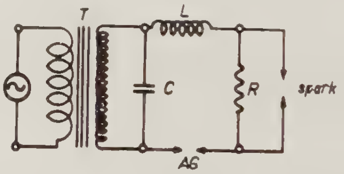

Fig. 6. Simple Circuit Diagram of the IG Spark

T—Transformer, C—Capacitance, L—Inductance, A.G.—Auxiliary gap, R—Resistance not releasing high frequency currents.

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# Physico-Chemical Characterization of Some 5,5-Disubstituted 1:3-Dimethyl Barbituric Acids

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### Abstract

Infrared spectra and ultraviolet characteristics for nine 5,5-disubstituted 1:3-dimethyl barbituric acids are presented. X-ray diffraction powder data are given for 5 of these compounds.

As part of a program of research comprising the synthesis of barbituric acid derivatives, a series of 1:3-dimethyl analogues was recently prepared in this laboratory. It is the purpose of this report to present the physico-chemical constants that were determined for the compounds.

## Experimental Results and Discussion

### Preparation and Purity

The 1:3-dimethyl derivatives of luminal, nembutal, seconal, and veronal were prepared by methylation of the acid in alkaline solution with methyl sulfate, according to the method of Bush and Butler (*1*). The remaining derivatives were methylated with diazomethane following the method of Dox (*2*). The barbituric acids used as starting materials were commercial samples obtained from reputable drug houses.

Several of the derivatives separated as oils that could not be induced to crystallize. These oils were dissolved in ether and washed repeatedly with dilute sodium hydroxide and water. The ether layer was filtered, and the solvent evaporated under reduced pressure. The derivatives, which separated as solids, were recrystallized to constant melting point. The melting points obtained for the derivatives of luminal and veronal agreed with those reported in the literature (*1,2*). The 1:3-dimethyl compounds of cyclopal, evipal, and rutonal, whose melting points had not been reported, were recrystallized from aqueous alcohol. Micro-Kjeldahl nitrogen determinations were performed on these three crystalline compounds and on those compounds which separated as oils. The results are shown in Table I.

### Infrared Data

Solid samples were prepared by grinding 2.5 mg of the derivative with 997.5 mg of KBr (A.C.S. reagent grade) in a Wig-l-bug amalgamator for 30 sec. Disks were obtained by pressing *in vacuo* 200 mg aliquots of the mixtures in a KBr disk die at 10,000 lbs/sq. in. for about 5 min. A disk containing only KBr was placed in the reference beam, and absorbancies of the disks containing the derivatives were measured over the wave number range of 4000-650 cm$^{-1}$. The spectra of the oils were taken as contact films. The spectra were recorded on a Perkin-Elmer Double Beam Model 21 Spectrophotometer equipped with rock salt optics, under standard conditions. The spectra are presented in Figures 1 and 2.

Marotta and Rosanova (*3*) have claimed that the N-methyl as well as the O-methyl derivative are generated during the methylation of barbital with diazomethane. Formation of the O-methyl derivative was later

TABLE I. PHYSICO-CHEMICAL CHARACTERISTICS OF 1:3-DIMETHYL DERIVATIVES OF BARBITURIC ACIDS

| *N-Methyl Derivative of* | | *Spectrum No.* | | | | *% N* | | *Ultraviolet Spectrum* | |
|---|---|---|---|---|---|---|---|---|---|
| *Trade Name* | *Chemical Name* | *Fig. 1* | *Fig. 2* | *Fig. 3* | *M. Pt. °C* | *Found* | *Calc.* | *λ max mμ* | *ε max* |
| Amytal | 5-Ethyl-5-isoamylbarbituric acid | 3 | — | — | oil | 10.60 | 11.02 | 224 | 6,431 |
| Cyclopal | 5-Allyl-5-(1-cyclopenten-2-yl) barbituric acid | — | 2 | 1 | 47.0—47.5 | 10.64 | 10.68 | 224 | 6,760 |
| Evipal | 5-(1-Cyclohexen-1-yl)-3,5-dimethyl barbituric acid | — | 1 | 2 | 76.5—77.5 | 11.16 | 11.19 | 225 | 5,745 |
| Luminal | 5-Ethyl-5-phenylbarbituric acid | — | 4 | 3 | 88.0—89.0 | — | — | 225 | 7,156 |
| Nembutal | 5-Ethyl-5-(1-methylbutyl) barbituric acid | 4 | — | — | oil | 10.64 | 11.02 | 225 | 6,230 |
| Neonal | 5-Ethyl-5-n-butylbarbituric acid | 2 | — | — | oil | 11.09 | 11.66 | 224 | 6,189 |
| Rutonal | 5-Methyl-5-phenylbarbituric acid | — | 3 | 4 | 98.0—99.0 | 11.06 | 11.37 | 226 | 7,332 |
| Seconal | 5-Allyl-5-(1-methylbutyl) barbituric acid | 5 | — | — | oil | 10.25 | 10.52 | 225 | 5,821 |
| Veronal | 5,5-Diethylbarbituric acid | 1 | — | 5 | 35.5—36.5 | — | — | 225 | 6,500 |

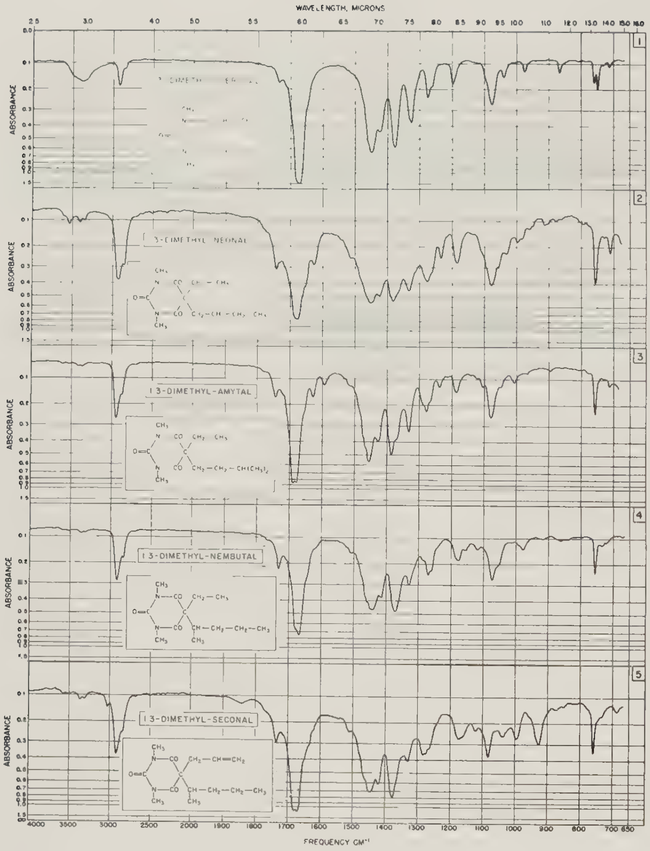

FIG. 1. INFRARED SPECTRA OF N-METHYL DERIVATIVES OF BARBITURIC ACIDS

questioned by Buch and Butler (*1*), Dox (*2*), and Stuckey (*4*) who reported the formation of N-methyl derivatives only when using diazomethane and/or methyl sulfate as methylating agents. The infrared data presented in Figures 1 and 2 support their findings based on chemical and ultraviolet spectral evidence. The spectra show clearly that the methylation process does not involve the carbonyl bonds but affects the imino linkages of the molecules (presence of C=O bands throughout 1650-1750 cm$^{-1}$ region; absence of N—H vibrations throughout 3100-3200 cm$^{-1}$ range). Reappearance of a strong absorption band in the 1360-1380 cm$^{-1}$ region affords further evidence for the presence of N—$CH_3$ bonds in this series of malonyl urea compounds.

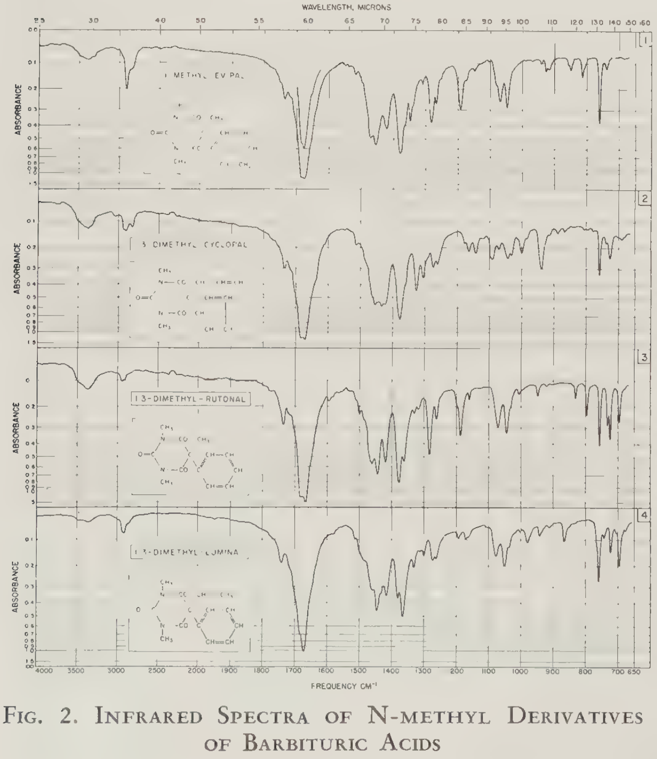

FIG. 2. INFRARED SPECTRA OF N-METHYL DERIVATIVES OF BARBITURIC ACIDS

## Ultraviolet Spectral Data

Solutions of the derivatives, 0.858-1.573 x 10$^{-4}$M, were prepared in alcohol and the ultraviolet spectra (200-360 m$\mu$) recorded on a Beckman DK-2 Automatic Spectrophotometer. Immediately after the spectrum was obtained, the cells were transferred to a Beckman DU Manual Spectrophotometer, and the absorbance measured at the wave length of maximum absorption. The data are listed in Table I. Attempts were made to obtain spectra in 0.01 *N* NaOH. The compounds were not readily soluble in alkali; however, upon adding 1 cc of alcohol to the sample and diluting to 200 cc with 0.01 *N* NaOH, the compounds dissolved readily. The spectra were recorded one min after the dilution had been completed. An absorption peak (228 m$\mu$) was observed only with the derivatives of nembutal and seconal. Stuckey (*4*) also noted no absorption peak for 1:3-dimethyl luminal and veronal in 0.01 *N* NaOH. However, Fox and Shugar (*5*) reported a peak at 228 m$\mu$ for 1:3-dimethyl veronal, which decreased 50% in 20 min. The $\varepsilon_{\max}$ for 1:3-dimethyl nembutal and seconal decreased very rapidly, approximately 40% within 2 min.

## X-Ray Diffraction Data

The x-ray diffraction patterns of the crystalline derivatives at room temperature were obtained. A standard preparation technique, as already reported (*6*), was used except in the case of the low melting point cyclopal and veronal derivatives whose powders could not be passed through the sieve. Diffraction patterns were obtained using Philips Debye-Scherrer cameras, diam. 114.83 mm, and Cu-K$\alpha$ radiation. A uniform exposure of 9 hrs at 33 kv and 15 ma was employed. Several patterns of the

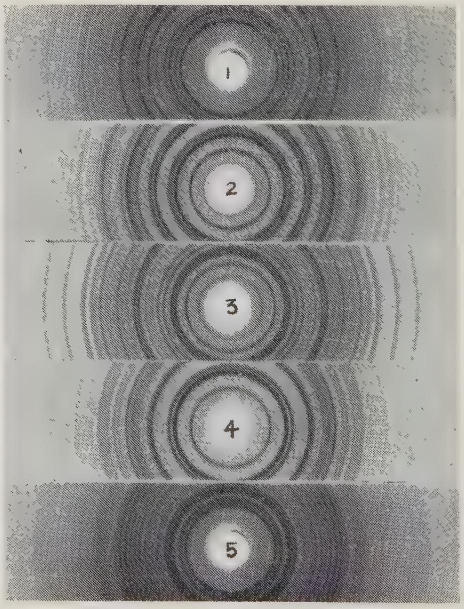

FIG. 3. X-RAY POWDER DIFFRACTION PATTERNS OF N-METHYL DERIVATIVES OF BARBITURIC ACIDS RECRYSTALLIZED FROM EITHER ALCOHOL OR ETHER
1—cyclopal, 2—evipal, 3—luminal, 4—rutonal, 5—veronal

Table II. Diffraction Data of 1:3-Dimethyl Derivatives of Barbituric Acids[a]

| *Cyclopal* | | *Evipal* | | *Luminal* | | *Rutonal* | | *Veronal* | |
|---|---|---|---|---|---|---|---|---|---|
| *d,A* | $I/I_0$ | *d,A* | $I/I_0$ | *d,A* | $I/I_0$ | *d,A* | $I/I_0$ | *d,A* | $I/I_0$ |
| 8.22 | 2 | 15.2 | 1 | 13.1 | 1 | 10.1 | 1 | 16.8 | 5 |
| 7.85 | 1 | 13.5 | 35 | 11.3 | 30 | 9.15 | 60 | 13.5 | 1 |
| 7.47 | 100 | 11.6 | 15 | 10.3 | 1 | 8.65 | 5 | 12.9 | 1 |
| 7.01 | 1 w | 9.88 | 2 w | 8.86 | 1 | 7.91 | 1 w | 9.17 | 1 |
| 6.66 | 40 | 9.11 | 60 | 8.10 | 70 | 7.10 | 2 w | 8.63 | 5 |
| 6.39 | 1 w | 8.23 | 2 w | 7.31 | 2 w | 6.61 | 60 | 8.11 | 100 |
| 6.10 | 100 | 7.25 | 25 | 6.57 | 95 | 6.37 | 100 | 7.56 | 28 |
| 5.84 | 1 w | 6.63 | 100 w | 6.35 | 20 | 6.16 | 2 | 7.20 | 55 |
| 5.61 | 50 | 6.37 | 5 | 6.11 | 100 | 5.84 | 80 w | 6.94 | 15 |
| 5.34 | 1 | 6.15 | 40 | 5.76 | 2 w | 5.59 | 1 | 6.65 | 2 |
| 5.19 | 1 | 5.89 | 50 | 5.42 | 60 | 5.42 | 1 | 6.28 | 50 |
| 4.97 | 35 | 5.34 | 2 w | 5.22 | 2 | 5.30 | 1 | 6.00 | 100 |
| 4.71 | 1 | 4.82 | 100 | 5.01 | 35 | 5.10 | 3 | 5.78 | 2 |
| 4.64 | 1 | 4.60 | 40 | 4.92 | 8 | 4.84 | 8 | 5.59 | 60 w |
| 4.48 | 75 | 4.46 | 50 | 4.72 | 3 | 4.60 | 70 | 5.36 | 2 |
| 4.37 | 1 | 4.31 | 2 | 4.62 | 10 | 4.47 | 80 | 5.18 | 15 |
| 4.27 | 1 | 4.19 | 3 | 4.47 | 15 | 4.34 | 40 | 4.95 | 25 w |
| 4.14 | 20 | 4.04 | 1 | 4.27 | 30 | 4.22 | 1 | 4.72 | 10 |
| 3.99 | 25 | 3.90 | 45 | 4.07 | 2 | 4.09 | 15 | 4.62 | 10 |
| 3.94 | 95 | 3.78 | 15 | 3.94 | 55 | 3.91 | 35 w | 4.43 | 20 |
| 3.83 | 1 | 3.70 | 5 | 3.86 | 2 | 3.80 | 25 | 4.27 | 40 |
| 3.75 | 35 | 3.61 | 35 | 3.77 | 85 | 3.72 | 35 | 4.04 | 2 d |
| 3.62 | 5 | 3.52 | 85 | 3.65 | 2 | 3.65 | 20 | 3.98 | 30 |
| 3.56 | 1 | 3.45 | 5 | 3.54 | 15 | 3.56 | 30 | 3.84 | 25 |
| 3.44 | 1 | 3.33 | 35 | 3.47 | 15 | 3.48 | 80 | 3.79 | 1 |
| 3.41 | 5 | 3.27 | 1 | 3.36 | 15 | 3.37 | 1 | 3.65 | 35 |
| 3.33 | 80 | 3.22 | 2 | 3.32 | 15 | 3.32 | 1 | 3.60 | 2 |
| 3.25 | 2 | 3.15 | 2 | 3.22 | 50 | 3.24 | 35 | 3.50 | 30 |
| 3.18 | 2 | 3.09 | 1 | 3.12 | 8 | 3.17 | 1 | 3.42 | 30 |
| 3.10 | 20 | 3.01 | 25 | 3.04 | 3 | 3.12 | 40 | 3.30 | 70 |
| 3.06 | 1 | 2.92 | 10 | 2.99 | 2 | 3.04 | 2 w | 3.22 | 5 |
| 3.01 | 1 | 2.85 | 50 | 2.94 | 10 w | 2.96 | 40 | 3.16 | 20 |
| 2.90 | 4 | 2.79 | 20 w | 2.85 | 1 | 2.89 | 20 | 3.10 | 1 |
| 2.86 | 1 | 2.72 | 15 | 2.81 | 50 | 2.84 | 5 | 3.04 | 1 |
| 2.82 | 1 | 2.67 | 10 | 2.79 | 3 | 2.79 | 30 | 2.99 | 2 |
| 2.77 | 10 | 2.59 | 10 w | 2.71 | 8 | 2.74 | 20 | 2.92 | 15 w |
| 2.72 | 10 | 2.56 | 10 w | 2.66 | 8 | 2.68 | 2 | 2.84 | 10 |
| 2.66 | 1 | 2.49 | 2 | 2.63 | 8 | 2.62 | 20 | 2.79 | 5 |
| 2.61 | 25 | 2.44 | 15 | 2.57 | 1 | 2.58 | 3 | 2.74 | 15 |
| 2.56 | 1 | 2.40 | 15 | 2.51 | 20 | 2.53 | 20 | 2.69 | 5 |
| 2.50 | 30 w | 2.33 | 2 | 2.47 | 8 | 2.48 | 15 | 2.64 | 5 d |
| 2.44 | 15 | 2.30 | 10 | 2.41 | 1 w | 2.43 | 10 | 2.55 | 5 d |
| 2.42 | 15 | 2.26 | 10 | 2.36 | 1 | 2.40 | 10 d | 2.53 | 8 |
| 2.36 | 10 d | 2.23 | 2 | 2.31 | 1 | 2.37 | 5 | 2.48 | 5 |
| 2.34 | 3 d | 2.19 | 10 | 2.28 | 1 w | 2.35 | 10 d | 2.44 | 15 |
| 2.29 | 2 w | 2.15 | 5 | 2.22 | 10 | 2.30 | 1 | 2.41 | 10 |
| 2.24 | 5 | 2.10 | 1 | 2.20 | 10 | 2.28 | 1 | 2.36 | 5 w |
| 2.23 | 5 | 2.08 | 8 | 2.17 | 5 w | 2.24 | 20 | 2.32 | 15 |
| 2.19 | 1 | 2.04 | 5 | 2.13 | 5 | 2.23 | 1 | 2.26 | 5 |
| 2.16 | 10 | 2.00 | 5 | 2.09 | 2 | 2.19 | 15 | 2.24 | 10 |
| 2.14 | 2 | 1.97 | 10 w | 2.05 | 5 | 2.17 | 1 | 2.20 | 5 |
| 2.09 | 2 | 1.94 | 5 | 2.00 | 2 | 2.14 | 12 | 2.18 | 5 |
| 2.08 | 5 | 1.91 | 5 | 1.98 | 10 w | 2.11 | 10 w | 2.13 | 10 |
| 2.03 | 20 | 1.89 | 10 d | 1.93 | 10 | 2.08 | 1 | 2.12 | 2 |
| 1.99 | 7 | 1.82 | 1 | 1.90 | 4 w | 2.05 | 35 | 2.09 | 1 |
| 1.97 | 5 | 1.80 | 15 | 1.87 | 1 | 2.01 | 1 | 2.07 | 8 |
| 1.95 | 2 | 1.78 | 2 | 1.84 | 3 | 1.99 | 1 | 2.03 | 10 |
| 1.93 | 1 | 1.76 | 10 | 1.81 | 4 | 1.97 | 5 | 2.00 | 2 |
| 1.90 | 3 d | 1.74 | 10 | 1.78 | 2 | 1.95 | 2 | 1.97 | 1 |
| 1.87 | 3 | 1.71 | 1 | 1.75 | 3 d | 1.93 | 20 w | 1.96 | 8 |
| 1.84 | 2 | 1.70 | 1 | 1.73 | 3 d | 1.88 | 2 | 1.92 | 8 |
| 1.81 | 1 | 1.67 | 2 | 1.69 | 8 | 1.86 | 5 w | 1.90 | 8 |
| 1.79 | 2 | 1.66 | 2 | 1.66 | 1 | 1.83 | 2 | 1.89 | 2 |
| 1.77 | 2 | 1.63 | 2 | 1.63 | 2 w | 1.80 | 1 | 1.85 | 1 |
| 1.74 | 1 | 1.59 | 1 | 1.55 | 1 | 1.78 | 10 | 1.81 | 1 |
| 1.73 | 1 | 1.58 | 1 | 1.54 | 2 | 1.77 | 1 | 1.76 | 2 w |
| 1.70 | 5 | 1.53 | 1 w | 1.52 | 1 | 1.75 | 2 | 1.74 | 1 |
| 1.67 | 8 w | 1.451 | 2 | 1.50 | 1 | 1.73 | 8 | 1.71 | 2 |
| 1.64 | 6 | 1.432 | 2 | 1.486 | 1 | 1.70 | 2 | 1.68 | 1 |
| 1.63 | 6 | 1.428 | 2 | 1.468 | 1 | 1.69 | 8 | 1.66 | 1 |
| 1.62 | 2 | | | 1.446 | 1 | 1.66 | 1 | 1.63 | 2 w |
| 1.61 | 2 | | | 1.426 | 2 | 1.65 | 1 | 1.58 | 1 |
| 1.59 | 1 | | | 1.389 | 1 | 1.64 | 1 w | 1.56 | 1 |
| 1.56 | 3 | | | 1.375 | 1 | 1.62 | 2 | 1.54 | 1 |
| 1.54 | 1 | | | 1.352 | 1 | 1.61 | 2 | 1.53 | 1 |
| 1.53 | 1 | | | | | 1.59 | 2 | 1.51 | 1 |
| 1.49 | 1 w | | | | | 1.58 | 2 | | |
| 1.47 | 1 | | | | | 1.56 | 1 | | |
| | | | | | | 1.55 | 2 | | |
| | | | | | | 1.53 | 5 | | |
| | | | | | | 1.51 | 1 | | |
| | | | | | | 1.493 | 12 | | |
| | | | | | | 1.467 | 1 | | |
| | | | | | | 1.462 | 1 | | |
| | | | | | | 1.456 | 1 | | |
| | | | | | | 1.445 | 1 w | | |
| | | | | | | 1.430 | 1 | | |
| | | | | | | 1.418 | 1 | | |
| | | | | | | 1.402 | 1 | | |
| | | | | | | 1.394 | 1 | | |
| | | | | | | 1.362 | 1 | | |
| | | | | | | 1.314 | 1 | | |
| | | | | | | 1.296 | 1 | | |
| | | | | | | 1.267 | 1 | | |
| | | | | | | 1.251 | 1 w | | |
| | | | | | | 1.240 | 1 | | |
| | | | | | | 1.232 | 1 | | |
| | | | | | | 1.216 | 1 | | |
| | | | | | | 1.204 | 3 | | |
| | | | | | | 1.181 | 1 | | |
| | | | | | | 1.512 | 1 | | |
| | | | | | | 1.136 | 1 | | |

[a] d, diffuse and w, wide
Cu-K$\alpha$, $\lambda = 1.54050$ A

derivatives recrystallized from 2 different solvents, alcohol and ether, were obtained to ascertain the reproducibility of the experimental data presented in Table II. No variation in the patterns shown in Figure 3 was observed.

## Acknowledgement

The authors are indebted to Dr. L. Levi for his continued interest in this project and for many useful discussions.

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* * *

# Note

## A Simple Method of Improving Sensitivity in the Infrared Determination of Sulfate*

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When alkali metal sulfates were ground with a slight excess of lead nitrate before incorporation in potassium bromide discs, the intensity of the S → O stretching frequency of 1115 cm$^{-1}$ was increased about tenfold. In the determination of alkali metal sulfates by infrared methods in this laboratory, sensitivity had been limited by the fact that their molar absorbances in 13-mm diam. potassium bromide discs were of the order of $10^3$ moles$^{-1}$.

The increased sensitivity is attributable to the metathesis of sulfate in the sample from the original state to lead sulfate. The apparent molar absorbances of the sulfates in potassium bromide discs vary with the associated cation, and lead sulfate is one of the most strongly absorbing. Since lead sulfate is also insoluble, it could be formed by grinding a sample of a soluble sulfate with a soluble lead salt in a slightly moist atmosphere.

The table shows the effect of grinding time and atmospheric moisture on the conversion. The extent of the conversion was determined by comparing the absorbance of the sample of sodium sulfate ground with lead nitrate with the absorbance of a stoichiometrically equivalent sample of reagent lead sulfate. It is seen that moisture in the atmosphere speeds up the reaction.

TABLE I. FORMATION OF $PbSO_4$ BY METATHESIS OF $Na_2SO_4$ AND $Pb(NO_3)_2$

| | *Extent of Conversion, %*[a] | |
|---|---|---|
| *Grinding Time, min* | *50% Rel. Humidity* | *5% Rel. Humidity* |
| 2 | 77 | 55 |
| 5 | 91 | 78 |
| 10 | 96 | 88 |
| 15 | 97 | 97 |

[a] Each % conversion is the average of duplicate runs. The range of deviations was about 2% for values of 90% or greater and up to 5% for some below 70%. Instrumental noise corresponded to approximately 2% conversion.

The metathesis must be effected before the sample is incorporated in potassium bromide. If a soluble sulfate, a soluble lead salt, and the potassium bromide are ground simultaneously, the large excess of bromide favors the formation of lead bromide rather than lead sulfate. After the formation of insoluble lead bromide, the lead is not available for the formation of lead sulfate.

Optimum conditions for sample preparation consisted of mixing the sample with a slight excess of lead nitrate in a stainless steel capsule. A stainless steel ball pestle was inserted and the capsule was vibrated on a dental amalgamator. After metathesis, potassium bromide was added to the capsule and the vibration was continued for 2 more minutes. The resulting mixture was pressed into a disc in the usual manner.

This method was applied successfully to the analysis of plutonium peroxide. When a 1-mg sample was used, less than 0.4 wt % of sulfate ion in plutonium peroxide was determined. The method can be applied to other anions in cases where an insoluble salt with the desired anion has a greater absorbance than soluble salts with the same anion.

Submitted June 14, 1960

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*The information contained in this note was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

†Present address: U. S. Atomic Energy Commission, Oak Ridge Operations Office, Oak Ridge. Tenn.

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# Spectrographic Tricks

## Long Path Infrared Microcell

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Midland, Michigan

The increasing demand for the analysis of trace organic chemicals in blood and urine by the solvent extraction technique described previously *(1)* has led to an investigation of methods to facilitate sample handling and improve efficiency *(2)*. In order to extend the method to the smaller laboratory animals it was found necessary to reduce the sample volume from 5 ml to 1 or 2 ml. In addition, it was desirable to take serial samples from an animal or human subject during the course of a chemical exposure so that changes of its concentration in the blood could be measured. This, too, necessitated smaller samples so that the total volume of blood lost would be minimized. The cell described below has a length of 10 mm and requires only 0.5 ml of solution. This gives a sensitivity of 1 - 10 ppm (minimum amount detectable) for many organic chemicals in a 1 ml sample of blood or urine.

Figure 1 shows a machine drawing of the cell. A ⅞-in. diam. rod is recessed on both ends to accommodate a ⅝-in. diam. window. A slot milled thru the center of the rod forms a sample chamber which is 10 mm in length and ⅛″ x ½″ in cross section. The cell itself does not vignette the beam of a Perkin Elmer Model 137 spectrometer when inserted into the microcell holder, but some losses result from reflection and scattering of the windows. The filling holes in the top of the cell are offset to permit the cell to slide fully into the microcell holder and are stoppered with small teflon plugs.

Two types of windows were tried; KBr pressed plates and AgCl discs. The former were cemented in place with an epoxy resin*, but it was difficult to obtain a good seal without getting some of the resin into the beam area. They also became cloudy after a short time as the solutions were saturated with water.

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*Araldite Type 102, with Hardener 951, Ciba Co., Inc., 627 Greenwich St., New York, N. Y.

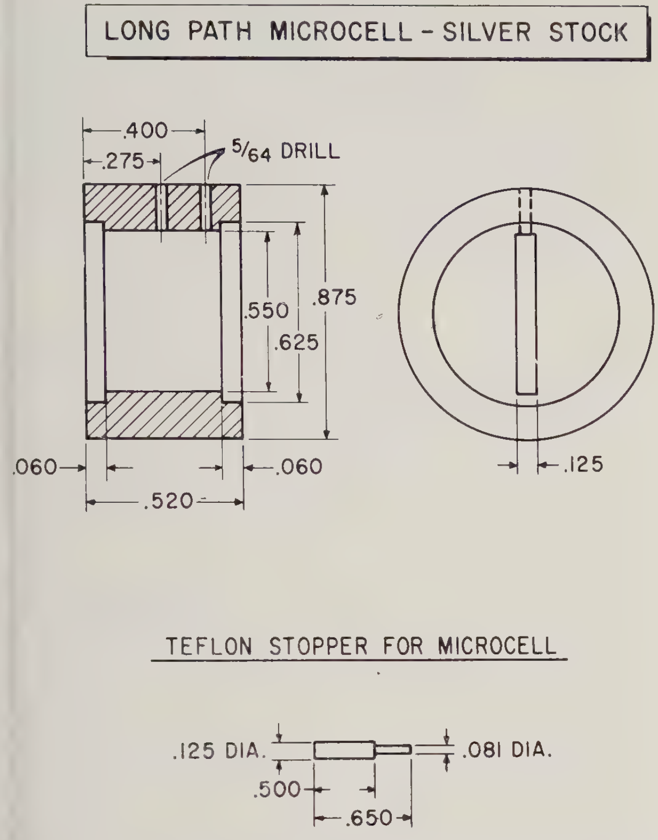

Fig. 1. Machine Drawing of Microcell. All Dimensions in Inches.

AgCl windows were cut with a No. 11 cork borer from a 1 mm sheet. Since AgCl is somewhat plastic, it may be sealed to the cell body by tapping the windows gently around the edge so that they spread out to form a pressure seal. The change in path length caused by slight distortions of the window is negligible in cells of 10 mm total length. A silver or Teflon cell body is used to prevent reaction of the silver chloride windows with metals higher in the electromotive series. Of these, silver (cost approximately $3.25/cell) has been found more satisfactory as it acts as a heat sink and minimizes the tendency of the solvent to boil in the cell. If Teflon is used, or for extended scans a silver cell, boiling may be virtually eliminated by placing a standard 1 mm cell filled with solvent between the source and the sample cell. This acts as a filter to remove that radiation which is causing the boiling.

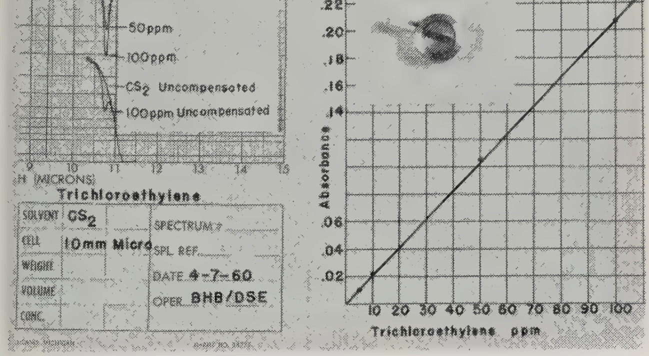

Fig. 2. Sensitivity and Analytical Performance of Microcell Used with Perkin Elmer Model 137 Spectrometer.

In practice a 2 ml blood sample is shaken for about 1 min with an equal volume of $CS_2$ and centrifuged to separate the layers. This yields enough solution to fill the cell twice. Satisfactory results can also be obtained using a 1 ml sample and 1 ml of solvent, but the agitation must be gentle to prevent excessive formation of emulsion. The spectra are usually obtained with a duplicate cell filled with solvent in the reference beam. This requires that the instrument slits be opened to regain the energy lost to solvent absorption. Figure 2 shows a series of standards scanned at the analytical wavelength for trichloroethylene, the resulting quantitative curve, and a photograph of the cell.

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Submitted May 10, 1960

* * *

## Heated Cell for Thermal Stability Studies of Polymers Using Infrared Spectroscopy*†

Robert T. Conley and Joseph F. Bieron
Department of Chemistry, Canisius College, Buffalo, New York

In the course of studies on the thermal stability of polymeric materials, it was of interest to follow the course of oxidative and non-oxidative degradation reactions of various functional groups in the polymers using infrared spectroscopy. In general, the method available for this type of investigation has been limited to heating the polymer sample in an oven followed by cooling of the specimen and determination of its infrared spectrum *(1)*. By successive heating and cooling cycles with intermittent spectral evaluation a series of spectra are obtained which are indicative of changes of functionality taking place under the degradative conditions. Recently *(2)*, the use of a heated wire cell has been reported for infrared studies of polymers up to 145°C. The advantage of this type of unit is that continuous monitoring of the sample is possible at the reaction temperature.

Sometime ago, in an effort to obtain kinetic data on polymer degradation reactions it was necessary to develop an infrared cell unit which could be used at temperatures from 100 to 400°C. The cell described here was constructed to the port dimensions of a Baird Model AB-2, double-beam, recording infrared spectrophotometer. However, using the same cell design, rectangular units have been constructed and used with equal success on other instruments.

As indicated in Figure 1, the entire cell unit is constructed of tempered asbestos. The heater unit is constructed from an aluminum tube (2½ in. dia., 1¼ in. long) covered on both sides with a thin layer of asbestos and wrapped with 9 ft. of chromel 'A' heating wire and an additional outer covering of asbestos tape. It has been found that the inner layer of asbestos is necessary in order

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*Presented at the 137th National American Chemical Society Meeting, Cleveland, Ohio, April 1960 and abstracted from the Masters' thesis of J. F. Bieron.

†This work was supported under Contract #DA-30-069-ORD-2626 and Grant #DA-ORD-31-124-60-G51 from the Office of Ordnance Research, U. S. Army.

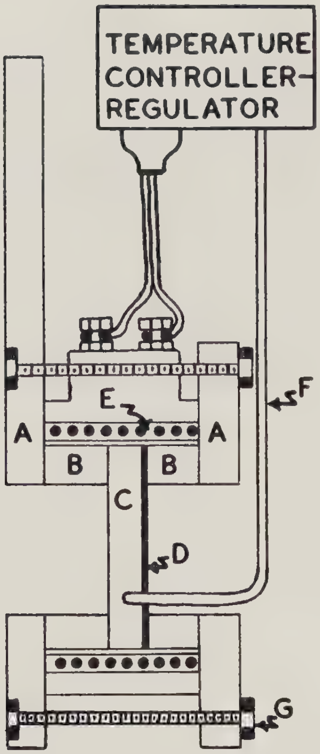

Fig. 1. Cell Assembly

A—Asbestos cell ends, B—Asbestos spacers, C—Salt plate, D—Polymer, E—Heating wire, F—Thermocouple, G—Retaining bolts.

to isolate the NaCl plate from the metal tube to prevent cracking of the salt plate on rapid heating and cooling. Although the cell ends can be fashioned from metal, such as brass or steel, asbestos markedly reduces the cost of the unit. In units for instruments which require a rectangular cell, a thin metal backing plate is necessary for repeated proper positioning of the cell on the instrument port.

The cell temperature is controlled and indicated through a single thermocouple positioned at one-half the radius of the salt disc. By using a proportioning controller-regulator unit with a 500 watt light bulb in the heating circuit in addition to the heater coil, temperature control is accurately maintained within ±2°C temperature range.

In the study of oxidative reactions in air, the cell was heated to reaction temperature under a cover of inert gas to prevent oxidation prior to the initial determination of the spectrum of the sample. Thereafter, the spectrum could be recorded of particular regions of interest as rapidly as desired. For example, on examination of the thermal degradation of polyacrylonitrile at 200°C the 4—7 micron region was scanned every 4 min for 6 hrs. At high temperatures, it has been found that it is necessary to adjust the base line with the sample inserted in the instrument at the reaction temperature in order to obtain good spectral data.

The same cell can be used for controlled atmosphere studies. The spacers, B, (Figure 1) are removed and a single spacer of asbestos is used between two salt discs. The polymer is on the inner face of the front plate. The gaseous atmosphere is passed through the chamber at a slow rate. The only modification is the insertion of two gas ports in the heater body. Using this technique it has been possible, for example, in helium atmospheres to trap out volatile degradation products for vapor phase chromatographic examination. This allows monitoring of both the gas and solid phases of the system during the degradation.

### Literature Cited

(1) B. D. Achlammer, M. J. Reiney, and F. W. Reinhart, J. Research Natl. Bur. Standards **47,** 116 (1951); A. L. Smith, L. H. Brown, L. J. Tyler, and J. M. Hunter, Ind. Eng. Chem. **49,** 1903 (1957)
(2) J. L. Luongo, J. Polymer Sci. **42,** 139 (1960)

Submitted August 25, 1960

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## Modifications to Spectrum Plate Comparator to View Overlapping Wavelength Ranges

H. P. Rothbaum and H. J. Todd
Dominion Laboratory, Wellington, New Zealand

With spectrographs of high dispersion it is impractical to record the whole spectrum from 2,000—10,000 A on one continuous photographic plate or film. For this reason many large spectrographs are made readily adjustable to focus any selected wavelength range on to a standard size photographic plate, generally 10″ x 4″. The situation can arise where plates exposed on different but overlapping wavelength ranges have to be compared, but the lateral adjustment on standard comparators is insufficient. In this laboratory an early model Judd-Lewis Comparator† has been permanently adapted and used for a number of years for this purpose. Figure 1 shows the attachment in position on a current model.

Lightweight open frames made of 1″ x ¼″ aluminum bar (1) replace the 10″ x 4″ spectrum plates in the Judd Lewis Comparator. The spectrum plates rest on these

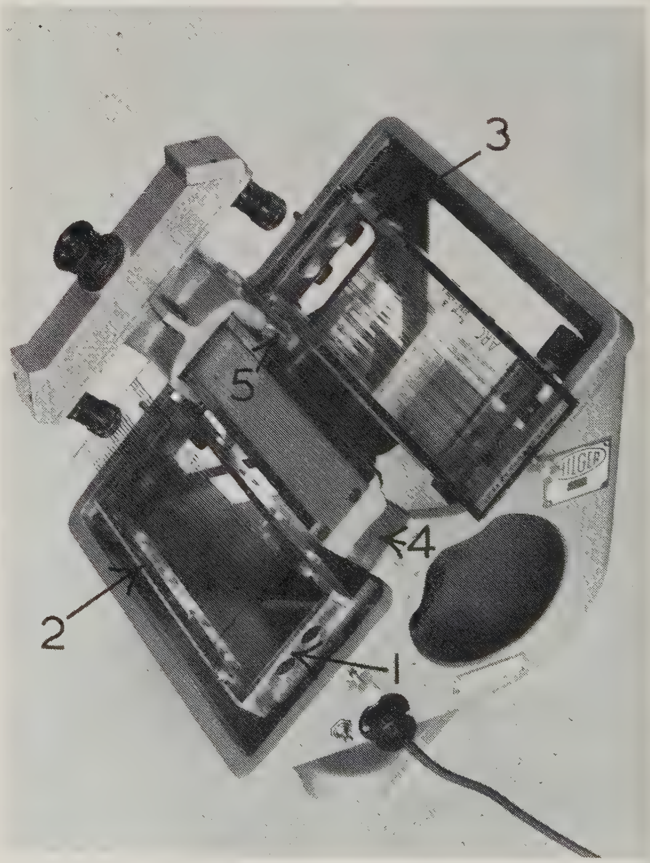

Fig. 1. Attachment in Position

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†A. Hilger, London, Engl.

frames, each being supported by a strip of aluminum (2) attached to the bottom of the frame. The plate is loosely clamped to the frame by microscope stage clips (3) fitting in holes drilled at regular intervals along the bars. To retain the same focal plane, the optical housing of the comparator is raised using two distance pieces of the same 1″ x ¼″ bar (4) and to give clearance the mirror assembly must be lowered by a similar amount (5). The frames can move vertically and the plates slide horizontally at least 4 in. in each direction. Plates of other sizes, e.g., quarter-plate and cracked or broken 10″ plates can readily be compared with standard plates. The body of the comparator prevents the lower exposures from entering the field of view so that the plate must be turned over for complete coverage. The small changes in dispersion when the same spectral region is exposed on different spectrograph ranges can be easily compensated by adjustment of one field lens.

Submitted August 15, 1960

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# Supplementary Optics For Perkin-Elmer Model 21, Double Beam Infrared Spectrophotometer

L. H. Little[†]

Department of Colloid Science, Free School Lane, Cambridge, England

While studying the infrared spectra of molecules adsorbed on solid surfaces, it was desirable to have the sample placed at a focal point in the infrared beam and not at the normal sample position used in the Model 21. Moreover the sample space in the instrument is 12 cm and it was necessary in this work to accommodate samples with path lengths up to 25 cm, when equipment was used for low or high temperature infrared studies. The simple optical system, shown in Figure 1(a), was constructed to meet these requirements. In Figure 2, the optical system, with a sample situated at the focus, is shown attached to the spectrometer.

A T-shaped piece of fibre board (Fig. 1(a)), ¾ in. thick, was cut to fit into the space between the source housing and the monochromator housing. By tightening screws at $G_1$ and $G_2$, covering holes in the base of the spectrometer, the fibre board was rigidly attached to the spectrometer.

$M_1$, $M_2$, $M_5$ and $M_6$ are plane front aluminized mirrors and $M_3$ and $M_4$ are front, aluminized, concave spherical mirrors, with apertures of 10 cm and radii of curvature, 26 cm and 28 cm, respectively. The distances between the centres of the mirrors are as follows: $M_1M_2 = 15$ cm, $M_2M_3 = 26$ cm, $M_3M_4 = 47$ cm, $M_4M_5 = 25$ cm, and $M_5M_6 = 13$ cm. Figure 1(b) shows the method of mounting the mirrors. The optical arrangement was designed to minimize the off-axis use of the spherical mirrors. The front, aluminized spherical mirrors[*] were inexpensive and were of the simple watch-glass type.

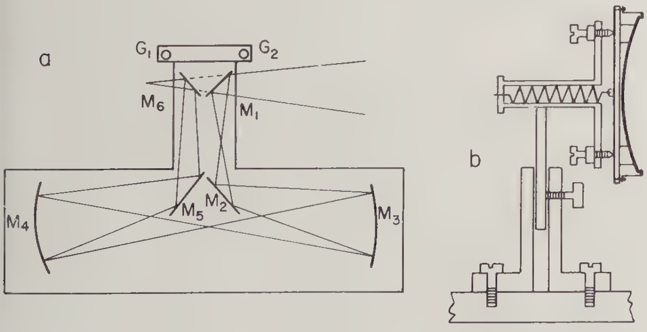

Fig. 1(a)—Supplementary Optical System,
(b)—Method of Mounting Mirrors

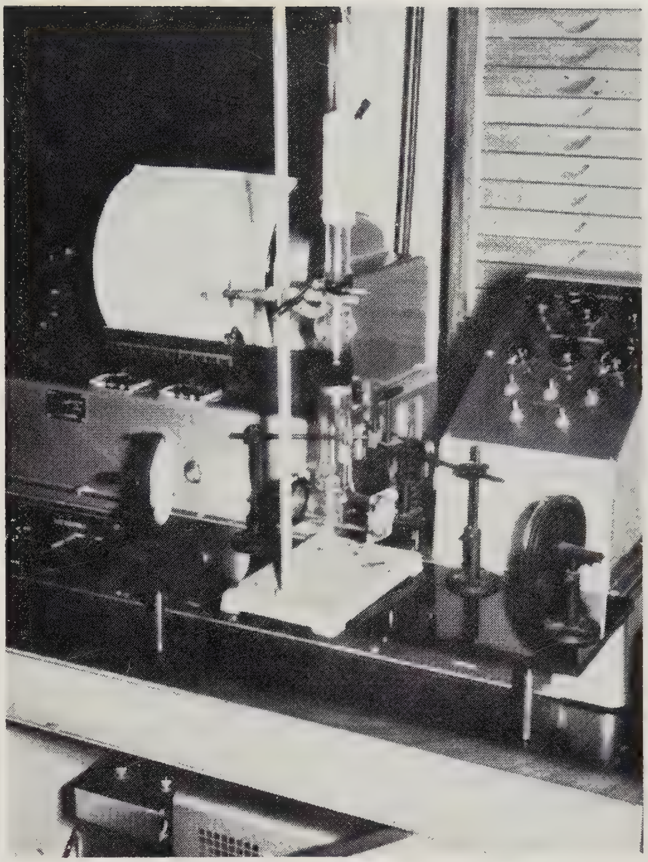

Fig. 2. Supplementary Optical System Attached to Spectrometer

In operation the complete optical unit may be attached to the spectrometer within a few min., the only adjustment necessary is to turn mirror $M_6$, about its vertical axis until maximum energy is obtained. When carefully focussed 70-75% of the incident energy is transmitted by the complete system. The spectrometer is returned to normal operation, simply by removing the supplementary optics. In regions of atmospheric absorption, there is incomplete compensation owing to the increased path length in the sample beam. However this absorption is not intense (15% absorption at the most intense lines in the water vapour spectrum) and allowance may be easily made for it by first recording a background spectrum.

The author is grateful to Dr. N. Sheppard for discussion and to Mr. J. Pratt for construction of the apparatus.

Submitted August 19, 1960

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[†] Present address: Dept. of Chemistry, University of Western Australia, Nedlands, Western Australia

[*] Supplied by Gowllands, Croydon, Engl., for less than $3 each.

# Infrared Quantitative Analytical Data

Starting with this issue, APPLIED SPECTROSCOPY will be publishing the Infrared Quantitative Analytical Data sponsored by the Coblentz Society. For the past three years these methods have appeared in Analytical Chemistry. The objectives of this program are:

1. To provide a medium for the publication of infrared analytical methods. Such methods represent original work but may not involve any new techniques.
2. To decrease the number of journal articles dealing with specific quantitative infrared analyses.
3. To acquaint analytical and other chemists with the scope of infrared as a quantitative analytical method.

It is not expected that the users of these methods could transfer all the data, including absorptivities, to his own instrument. Rather, the methods would serve as a guide to the establishment of his own analytical parameters and would indicate the probable accuracy of the determination.

It should be emphasized that the infrared methods represent original contributions to the permanent literature. Before publication, the methods are reviewed by a committee of infrared experts from the Society. Methods which are considered satisfactory and useful are then prepared for publication.

The program is not intended to preclude regular publications. If the method is sufficiently unique that it cannot adequately be described using the standard format, a full article should be submitted in the normal manner.

Publication is open to any person and is not limited to members of the Coblentz Society or the Society for Applied Spectroscopy. Contributions should be sent directly to the Chairman of the Review Committee, Dr. A. Lee Smith, Spectroscopy Laboratory, Dow Corning Corporation, Midland, Michigan. It is requested that methods be submitted in quintuplicate, using the standard format. Infrared spectra cannot be published as a part of this program.

## Explanation of Form

*Title* This is a brief statement of the component(s) of the mixture for which analysis is desired.

*Components* The components are listed in accordance with the International Union rules for nomenclature.

*Empirical Formula* Given for ease in indexing.

*Concentration Range* The range over which the analysis is applicable is stated.

*Accuracy* This can be reported in several ways, including standard deviation, coefficient of variation, relative error, or absolute error. The author should make clear which system he is using.

*λ or ν—B.L. Points* The analytical wavelengths (λ) or wavenumber (ν) values are given as accurately as possible. The B.L. (base line) points are also given below the λ or ν value if the base line is determined by a line connecting two abscissa values. If it is drawn tangent to an arbitrary spectral slope, the fact is noted under Comments.

*Slit Width* The mechanical slit width, if known, is given in mm. A calculated value for the spectral slit width has been requested previously, but this figure is no longer required.

*Concentration-Length* The concentration of the analyzed sample in solvent and the cell length are given for each point. If these data are constant, they are stated once and dittoed thereafter.

*Instrument* The make and model of the instrument is stated together with the prism material used.

*Sample Phase* This describes sample conditions—i.e., solution, gas, KBr disc, etc.

*Absorbance Measurement and Concentration* The method used is checked.

*Absorptivities* Analytical Matrix. Relative absorbances are given as the slope of the Beer's law concentration curves used, expressed in terms of absorbance per 100% of constituent.

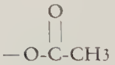
*Material Purity* The probable purity of the reference material and the source, if commercially available, is stated.

*Comments* This covers any unusual points such as special sampling precautions, special treatment of $I_0$ reference signal, methods that are not standard, etc. Whenever possible, a literature reference is preferred to an explanation.

## Determination of Acetyl Content of Secondary Cellulose Acetate

**C. D. BOCKMAN, JR., Tennessee Eastman Company, Kingsport, Tennessee**

**CS-150**

| *Component* | | | *Range* | *Accuracy* | *λ or ν* | | *Conc.* |
|---|---|---|---|---|---|---|---|
| *No.* | *Name* | *Formula* | *%* | *%* | *B.L. Pts.* | *Slit* | *Length* |
| 1 | Acetyl |  $-O-C(=O)-CH_3$ | 33-44 | ± .9 | 5.8μ | S.F. = 1 | 2.0<br>.100 |

*Instrument:* Baird Atomic Inc., Model KM-1, NaCl Prism

*Sample Phase:* Solution in $CH_2Cl_2$: MeOH (9:1)

*Cell Windows:* NaCl

*Absorbance Measurement:* Base line......X...... Point............

*Calculation:* Inverted Matrix............ Successive Approx............ *Graphical*.....X.....

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | 5.8μ |
|---|---|
| 1 | .0280 |

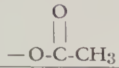
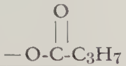
*Material Purity:* Reference compounds are approximately 99% pure cellulose ester.

*Comments:* The relative absorbance is given as the slope of the Beer's Law concentration curve used. This curve passes through zero absorbance at 10% acetyl content.

## Determination of Acetyl and Butyryl Content of Cellulose Acetate-Butyrate Esters

**C. D. BOCKMAN, JR., Tennessee Eastman Company, Kingsport, Tennessee**

**CS-151**

| Component | | | Range | Accuracy | λ or ν | Slit | Conc. |
|---|---|---|---|---|---|---|---|
| No. | Name | Formula | % | % | B.L. Pts. | | Length |
| 1 | Acetyl |  $-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|\|}}{\mathrm{C}}-\mathrm{CH_3}$ | 5-30 | ±1.0% | 8.1μ | S.F.=1 | 0.5% in KBr<br>0.031″<br>in die |
| 2 | Butyryl |  $-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|\|}}{\mathrm{C}}-\mathrm{C_3H_7}$ | 15-50 | ±1.0% | 8.6μ | S.F.=1 | " |

*Instrument:* Baird Atomic Inc., Model KM-1, NaCl Prism

*Sample Phase:* Solid in KBr

*Cell Windows:*

*Absorbance Measurement:* Base line......X...... Point...........

*Calculation:* Inverted Matrix........... Successive Approx.......... *Graphical*......X......

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | *8.1μ* | *8.6μ* |
|---|---|---|
| 6% Ac-48.3% Bu | 0.283 | 0.717 |
| 13.6% Ac-37.3% Bu | 0.640 | 0.360 |
| 22.2% Ac-25.6% Bu | 0.854 | 0.146 |
| 24.0% Ac-23.8% Bu | 0.888 | 0.112 |
| 30.3% Ac-16.7% Bu | 0.944 | 0.056 |

*Material Purity:* Reference compounds are approximately 99% pure cellulose ester.

*Comments:* Relative absorbances are expressed as fractions of the sum of the two absorbances, (A at 8.1μ + A at 8.6μ = sum) and equal A at 8.1μ or 8.6μ/sum. The individual data are presented since a straight line relationship is not obtained.

## Determination of Ethyl Alcohol in Acetone

**RAY L. JACKSON, Tennessee Eastman Company, Kingsport, Tennessee**

**CS-152**

| Component | | | Range | Accuracy | λ or ν | Slit | Conc. |
|---|---|---|---|---|---|---|---|
| No. | Name | Formula | % | % | B.L. Pts. | (mm) | Length |
| 1 | Ethyl Alcohol | $C_2H_5OH$ | 0-15% | ± .25 | 2.05μ | 0.090 | 100%<br>1 cm |

*Instrument:* Beckman DK-1, Quartz Prism

*Sample Phase:* Liquid, full strength

*Cell Windows:* Quartz or Corex

*Absorbance Measurement:* Base line........... Point......X......

*Calculation:* Inverted Matrix........... Successive Approx............ *Graphical*......X......

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | *2.05μ* |
|---|---|
| 1 | 4.77 |

*Material Purity:* 99+% pure

*Comments:* The absorbance measurement is made on acetone containing ethyl alcohol varying from 0-15%. Ethanol free acetone is used as the reference.

## Determination of Water in Acetone

**RAY L. JACKSON, Tennessee Eastman Company, Kingsport, Tennessee**

**CS-153**

| Component | | | Range | Accuracy | λ or ν | Slit | Conc. |
|---|---|---|---|---|---|---|---|
| No. | Name | Formula | % | % | B.L. Pts. | (mm) | Length |
| 1 | Water | $H_2O$ | 0-3 | ± .06% | 1.44μ | 0.030 | 100%<br>1 cm |

*Instrument:* Beckman DK-1, Quartz Prism

*Sample Phase:* Liquid, full strength

*Cell Windows:* Quartz or Corex

*Absorbance Measurement:* Base line........... Point......X......

*Calculation:* Inverted Matrix........... Successive Approx............ *Graphical*.....X......

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | *1.44μ* |
|---|---|
| 1 | 11.2 |

*Material Purity:* 99+% pure

*Comments:* The absorbance measurement is made on acetone containing water varying from 0-3%. 99.97% acetone (0.03% water) is used as reference.

## Determination of β-Naphthylamine in α-Naphthylamine

**M. F. GROSTIC and G. E. BRONSON, The Upjohn Company, Kalamazoo, Michigan**

**CS-154**

| Component | | | Range | Accuracy | λ or ν | Slit (mm) | Conc. |
|---|---|---|---|---|---|---|---|
| No. | Name | Formula | % | % | B.L. Pts. | Δλ or Δν | Length |
| 1 | α-Naphthylamine | $C_{10}H_9N$ | 95-100 | ± 1 | 11.6μ | 0.216<br>0.034 | 52.5<br>mg/ml<br>0.5 mm |
| 2 | β-Naphthylamine | $C_{10}H_9N$ | 0-5 | ± 1 | 11.86μ | 0.231<br>0.036 | " |

*Instrument:* Perkin-Elmer Model 21, NaCl Prism

*Sample Phase:* Solution in Acetone

*Cell Windows:* NaCl

*Absorbance Measurement:* Base line........... Point.....X......

*Calculation:* Inverted Matrix .....X ..... Successive Approx........... *Graphical*.............

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | *11.6μ* | *11.86μ* |
|---|---|---|
| 1 | 0.513 | 0.269 |
| 2 | 0.872 | 2.864 |

*Comments:* β-Naphthylamine has been implicated in animal studies as a causative agent in bladder papilloma and should be handled with great care. See *Papilloma in the Bladder in the Chemical Industry,* a booklet issued by The Association of British Chemical Manufacturers, 166 Piccadilly, London, 1953.

## Determination of 11α-Hydroxyprogesterone

**M. F. GROSTIC and G. E. BRONSON, The Upjohn Company, Kalamazoo, Michigan**

**CS-155**

| Component | | | Range | Accuracy | λ or ν | Slit (mm) | Conc. |
|---|---|---|---|---|---|---|---|
| No. | Name | Formula | % | % | B.L. Pts. | Δλ or Δν | Length |
| 1 | 11α-Hydroxyprogesterone | $C_{21}H_{30}O_3$ | 90-100 | ± 1 | 10.24<br>9.95<br>and<br>10.38μ | 0.169<br>0.026 | 60<br>mg/ml<br>0.5 mm |

*Instrument:* Perkin-Elmer Model 21, NaCl Prism

*Sample Phase:* Solution in Chloroform

*Cell Windows:* NaCl

*Absorbance Measurement:* Base line.....X...... Point ...........

*Calculation:* Inverted Matrix........... Successive Approx............ *Graphical*.....X......

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | *10.24μ* |
|---|---|
| 1 | 0.272 |

*Material Purity:* Reference compound 99.5% pure.

*Comments:* 9.95 and 10.38 μ are the tangent points for the base line.

*(Continued on page 88)*

# Book Review

**X-Ray Absorption and Emission in Analytical Chemistry** by H. A. Liebhafsky, H. G. Pfeiffer, E. D. Winslow, and P. D. Zemany, John Wiley & Sons, Inc., New York, 1960, 357 pp., $13.50

Within the past few years, as the art and science of x-ray fluorescence spectroscopy has rapidly advanced, there has been a noticeable void in textbooks in this field. Now, however, within a very short time, two such texts have been forthcoming, this being the second of the two, and a very good one.

The preface sets the pace: "...with the analytical chemist in mind, we have not treated all topics equally. The electronics expert is likely to feel we have skimped . . .; statisticians will find much missing . . .". Many men having had their education and training in the field of analytical chemistry, suddenly find themselves thrust into x-ray fluorescence spectroscopy. With little written information to guide them, they grope in the darkness, not even understanding the principals of the field in which they are now working. With this in mind, the authors have planned this book so that those with their interest limited to a particular field may easily find in the various chapters such specific information as the history and theory of x-ray methods; measurement of intensity and detectors; absorptiometry with polychromatic or monochromatic beams; film thickness determinations; x-ray emission spectrography; notes on equipment; reliability; and so on. This breakdown by chapters makes it easy for those not familiar with x-ray methods to find the information he desires very quickly.

The seven appendices contain tables of value to those working with x-ray spectroscopy, namely critical absorption edges and energies, approximate intensities of x-ray lines, wavelengths of characteristic lines, mass absorption coefficients, relation of wavelengths to diffraction angle for various crystals. The final appendix, which deals with safety, wisely cautions, not only about the danger of radiation but also concerning the high voltages used.

In writing Chapter 9, "Notes on Equipment. Representative Spectrographs", the authors have shown excellent restraint. As employees of a company manufacturing x-ray equipment they could easily, and understandably, have shown partiality to the equipment their company manufactured. However, they are to be complimented on the objective approach they have made in reviewing the various instruments available.

From Chapter 1, "Origin and Properties of X-Rays", all the way through, this book is well-written, and makes for easy reading. The authors seem to have made every effort to make its contents understandable to those who have had no specific training in this particular field.

*G. L. Crumrine*

# Society News

## International Conference on Spectroscopy

College Park, Md. June 18-22, 1962

The Program Committee of the International Conference on Spectroscopy for 1962 has been active in planning the Conference Program. The Committee is of the opinion that there should be a strong program of invited papers. This will be accomplished by confining the submitted papers to selected themes or a small range of topics.

The themes to be considered are:

*Atomic Emission and Absorption*

Sample volatilization mechanisms and excitation processes, new excitation techniques, time resolved spectroscopy, vacuum spectroscopy, wavelength standards, term analyses.

*Astrophysical*

Abundance of the elements in the sun and stars, rocket spectroscopy, transition probabilities.

*Infrared, Raman, and Microwave*

Applications of high resolution, interferometers, environmental effects and intensities, new trends in Raman sources, wavelength standards.

*Mass*

Metals, alloys and refractory materials, correlations of spectra with structure.

*Magnetic Resonance*

Applications of new NMR techniques to chemical problems, oriented free radicals, irradiated materials, and high resolution EPR spectra, triplet states, nuclear magnetic spectra of nuclei other than hydrogen and fluorine, transition metal complexes.

*Ultraviolet and Visible*

Optical masers, reflection spectra, inorganic chemistry and crystal field spectra, high pressure and temperature techniques, fluorescence spectra.

*X-ray Emission and Absorption*

Microprobes, emission from light elements, emission from complex samples, unconventional methods and experiments, absorption edge and oxidation state studies.

*Education*

Teaching methods, history, laboratory equipment and experiments.

### Program Committee

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*Astrophysical:* Dr. Richard Tousey, Naval Research Laboratories, Washington

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*Mass:* Dr. V. H. Dibeler, National Bureau of Standards, Washington

*Magnetic Resonance:* Prof. C. Hutchinson, University of Chicago

*Ultraviolet and Visible:* Dr. R. A. Friedel, Bureau of Mines, Pittsburgh

*X-ray Absorption and Emission:* Dr. H. A. Liebhafsky, General Electric Research Laboratory

*Education:* Prof. E. J. Rosenbaum, Drexel Institute of Technology

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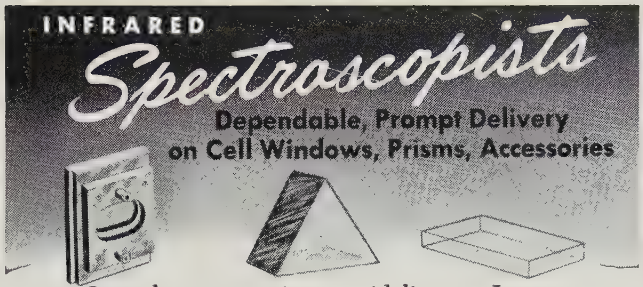
*Magnetic Resonance:* Dr. H. C. Allen, National Bureau of Standards

*X-ray Emission and Absorption:* Dr. I. Adler, U. S. Geological Survey, Washington

*Education:* Dr. Mary E. Warga, Optical Society of America

Submitted papers should emphasize new methods, unconventional experiments, and trends in applications of spectroscopy. The limited program time will not allow for descriptions of analytical methods based on well known practices and techniques.

Those desiring to present papers should submit titles and abstracts of 300 words or less to the Conference Chairman before December 1, 1961. All individuals interested in further details should send their names and address to: Mr. Bourdon F. Scribner, General Chairman, International Conference on Spectroscopy, National Bureau of Standards, Washington 25, D.C., U.S.A.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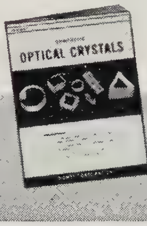

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# S.A.S. Local Section News

Editor—Carl J. Leistner

**[Items for this column should be sent to the Editor, Mr. Carl J. Leistner, United Carbon Products Company, P. O. Box 747, Bay City, Michigan.]**

### Eastern Analytical Symposium

Hotel Statler Hilton November 15-17, 1961

In a continuing effort to provide an outstanding program of specialized topics in Analytical Chemistry, comprehensive symposia will once again be presented by well known industrial researchers and academic leaders in the field. Dr. Saul Gordon of Fairleigh Dickinson University is General Chairman, and Dr. Eugene Rosenbaum of Drexel Institute of Technology is Program Chairman.

The Symposium Governing Board, at this time, is very proud to announce that the following sums have been donated to the parent societies of the sponsoring groups to aid their individual efforts:

(1) \$500 to the Division of Analytical Chemistry of the American Chemical Society to cover the expenses of sponsored speakers.
(2) \$500 to the Metropolitan Microchemical Society to meet expenses of the International Symposium on Microchemical Techniques, to be held at Penn State University, August 13-18.
(3) \$500 to the Society for Applied Spectroscopy for its journal, Applied Spectroscopy.

### Baltimore-Washington Section

*George E. Ashby* has been elected Chairman for 1961-2. He has served as Secretary of the Section since 1959 and also is currently Publicity Chairman for the International Conference on Spectroscopy to be held at the University of Maryland in 1962.

Mr. Ashby studied at George Washington University and the University of Maryland, from which school he received a B.S. in Physics. Since 1957, he has been Senior Research Physicist at the Washington Research Center of the W. R. Grace & Co. in charge of the x-ray and electron microscopy laboratories.

Other officers elected included; Vice-Chairman, Franklin R. Winter, Koppers Co., Baltimore, Md., Secretary, Sally F. Mount, Baltimore Gas & Electric Co., Baltimore, Md., and Treasurer, Harry J. Rose, U. S. Geological Survey, Washington, D.C.

*(Continued on page 15A)*

# News of Other Societies and Institutions

[Contributions to this column should be sent to the Editor, Mr. Raymond R. Sawyer, Columbia University, Hudson Laboratory, Dobbs Ferry, N. Y.]

## Infrared Spectroscopy Institute at Canisius College

Buffalo, N. Y. August 14-18, 1961

For the fifth year Canisius College will offer a five day course on various aspects of infrared, Raman, and nuclear magnetic resonance spectroscopy. The nineteen-man staff includes six specialists from college faculties, six representatives of leading instrument manufacturers, and seven industrial spectroscopists. For further information, contact Dr. Herman A. Szymanski, Director, Infrared Spectroscopy Institute, Canisius College, Buffalo 8, N. Y.

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## Course in Modern Industrial Spectroscopy at Arizona State University

Tempe, Arizona August 21-September 1, 1961

Lecturers will include members of the Departments of Chemistry and Physics at Arizona State University and invited guest speakers from industrial laboratories. For further information, contact Dr. Jacob Fuchs, Director, Modern Industrial Spectroscopy, Arizona State University, Tempe, Arizona.

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## Future International Meetings

## Colloqium on Optical Materials

Paris July 5-8, 1961

Sponsored by International Commission for Optics.

Contact Institut d'Optique, 3, boul. Pasteur, Paris 15e, France.

## Conference on Optical Instruments and Techniques

London July 10-14, 1961

Sponsored by International Commission for Optics and British National Committee for Physics

Contact K. J. Habell, National Physical Laboratory, Teddington, Middlesex, England

## Conference on Radiofrequency Spectroscopy in Solids

Bangor, Wales September 21-22, 1961

Sponsored by Physical Society, Solid State Group and Radiofrequency Spectroscopy Group

Inquire at Physical Society, 1 Lowther Gardens, Prince Consort Rd., London, S.W. 7, England

## International Commission for Optics, General Assembly, 6th

Munich August, 1962

Sponsored by International Commission for Optics

Contact Prof. W. D. Wright, Technical Optics Section, Imperial College, London, S.W. 7, England

## Symposium on Spectroscopy

Tokyo 1962

Contact Dr. Rudolf Morf, Secretary General, International Union of Pure and Applied Chemistry, c/o Sandoz Ltd., Basel 13, Switzerland

*(Continued on page 15A)*

**Infra-Red Data—** *(Continued from page 85)*

### Determination of Iso-3-ketobisnor-4-cholen-22-al in 3-Ketobisnor-4-cholen-22-al

**M. F. GROSTIC and G. E. BRONSON, The Upjohn Company, Kalamazoo, Michigan**

**CS-156**

| *Component* | | | | | | | |
|---|---|---|---|---|---|---|---|
| *No.* | *Name* | *Formula* | *Range %* | *Accuracy %* | *λ or ν B.L. Pts.* | *Slit (mm) Δλ or Δν* | *Conc. Length* |
| 1 | Iso-3-keto-bisnor-4-cholen-22-al | $C_{22}H_{31}O_2$ | 25-100 | ± 1.5 | 11.24μ | 0.198<br>0.036 | 25 mg/ml<br>1.0 mm |
| 2 | 3-Ketobisnor-4-cholen-22-al | $C_{22}H_{31}O_2$ | 25-100 | ± 1.5 | 11.24μ | 0.198<br>0.036 | ,, |

*Instrument:* Perkin-Elmer Model 21, NaCl Prism

*Sample Phase:* Solution in Methylene Bromide

*Cell Windows:* NaCl

*Absorbance Measurement:* Base line........... Point......X.....

*Calculation:* Inverted Matrix......X...... Successive Approx...... *Graphical*...........

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | *11.24μ* |
|---|---|
| 1 | 0.289 |
| 2 | 0.167 |

*Material Purity:* Reference compounds 98+% pure.

*Comments:* Procedure valid for the known two-component system. It is applicable because the compounds are isomeric and make up the total sample. Results are calculated by use of the following equation:

$$\% \times = 100\ (\text{Absorbance of Sample} - k_y)/k_x - k_y$$

### Determination of N-(β-Hydroxyethyl) phenylacetamide, Ethanolamine, and Methyl Phenylacetate in Mixtures

**M. F. GROSTIC and G. E. BRONSON, The Upjohn Company, Kalamazoo, Michigan**

**CS-157**

| *Component* | | | | | | | |
|---|---|---|---|---|---|---|---|
| *No.* | *Name* | *Formula* | *Range %* | *Accuracy %* | *λ or ν B.L. Pts.* | *Slit (mm) Δλ or Δν* | *Conc. Length* |
| 1 | N-(β-Hydroxyethyl) phenylacetamide | $C_{10}H_{12}O_3$ | 90-100 | ± 1 | 6.03μ | 0.130<br>0.035 | 20 mg/ml<br>0.2 mm |
| 2 | Methyl Phenylacetate | $C_9H_{10}O_2$ | 0-10 | ± 1 | 5.77μ | 0.130<br>0.032 | ,, |
| 3 | Ethanolamine | $C_2H_9ON$ | 0-10 | ± 1 | 6.32μ | 0.130<br>0.036 | ,, |

*Instrument:* Perkin-Elmer Model 21, NaCl Prism

*Sample Phase:* Solution in Chloroform

*Cell Windows:* NaCl

*Absorbance Measurement:* Base line........... Point......X ...

*Calculation:* Inverted Matrix......X...... Successive Approx............ *Graphical*...........

*Relative Absorbances—Analytical Matrix:*

| *Component/λ* | *6.03μ* | *5.77μ* | *6.32μ* |
|---|---|---|---|
| 1 | 0.721 | 0.017 | .058 |
| 2 | 0.022 | 0.750 | .043 |
| 3 | 0.033 | 0.020 | .190 |

*Material Purity:* Reference Compounds 98% Pure.

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**What's New—** *(Continued from page 7A)*

10th. OSA is making this special offer to members of some sixty scientific societies across the English speaking world, and it asks the members of those Societies to write to their Society or directly to the Assistant Secretary, OSA, 1155 16th St., N.W., Washington 6, D.C. for further details or to send in their order.

One thing that has been learned from Optics and Spectroscopy is that the majority of the references cited are to English language journals.

——— λ ———

The Optical Society of America will also publish *Applied Optics*. It will publish work in the areas of applied optics and closely related scientific and technical fields. This publication is devoted solely to applied optics in its broadest phases and designed to meet the interests of scientists, engineers, technologists, and technicians working in optics or its applications, in fields borderline to optics and employing optical techniques.

The Subscription rates are:

| | |
|---|---|
| OSA Members | $6.00 per year |
| Other AIP Societies Members | $8.00 per year |
| Non members | $10.00 per year |

For information, contact the Optical Society of America, 1155 16th St., N.W., Washington 6, D.C.

——— λ ———

The first cumulative index of the *Index Chemicus* marks the first time that the vital information on 75,000 new chemical compounds has been reported so promptly. The Index Chemicus was prepared by electronic computing equipment in record-breaking time. Prior to the introduction of Index Chemicus in August 1960, chemists had to wait from two to five years to obtain this same information from conventional abstracting services. Now this vital information is available within sixty days. Index Chemicus contains listings of chemical names, structural diagrams, and molecular formulas; as well as complete bibliographical information, including article titles, authors, institutions, addresses, and original journal references. For further information, contact the Institute for Scientific Information, 33 South Seventeen Street, Philadelphia 3, Pa. ....

——— λ ———

Everyone who uses an infrared spectrometer needs to establish or to check its *wavelength calibration.* Many workers, indeed, should check it more often than they do. Over the past twenty years, a number of convenient unofficial standards have come to be

*(Continued on page 15A)*

ARL offers
"COMPLETE" ECONOMY
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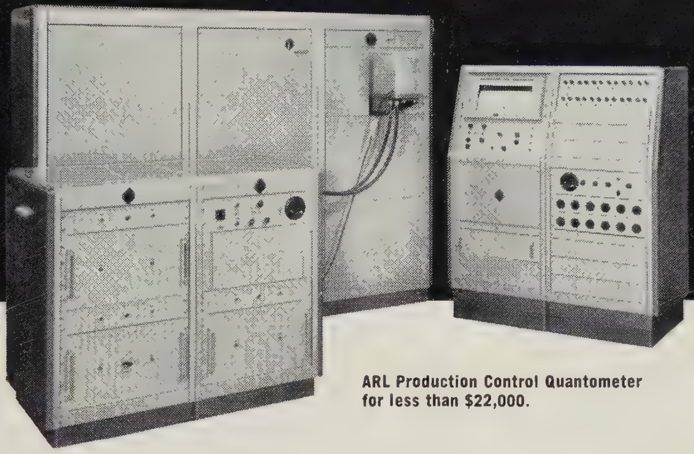

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ECONOMY OF DESIGN—ARL's Production Control Quantometer laboratory provides maximum flexibility for changes in analytical programs. Model 29000 Spectrometer can accommodate 48 phototubes, making possible 48 simultaneous analytical determinations. A choice of one of the three available high-dispersion quartz gratings (960, 1200, 1440 lines/mm) provides optimum dispersion for any analytical requirement. The recording console is readily adaptable for use with ARL x-ray fluorescence analyzers at a substantial savings in new equipment.

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**UNION CARBIDE**

**Local Section News—** *(Continued from page 87)*

### Pittsburgh Section

To encourage the study of spectroscopy, the Pittsburgh Section has given nine grants to area colleges, since a monetary award program was begun in 1957. This year, twenty-three colleges submitted proposals for a college grant. The recipients for the awards, each to receive $1500, will be Musgingum College, New Concord, Ohio, and Thiel College, Greenville, Pa. The award money will be used to purchase spectrographic equipment. The awards were presented at the monthly meeting of the Section on April 19, 1961, at Mellon Institute, Pittsburgh, Pa.

### Gift to the Journal

Applied Spectroscopy acknowledges with gratitude the gift of $500 from the Eastern Analytical Symposium.

**Applied Spectroscopy is soliciting Classified Advertising relating to employment opportunities, situations wanted, used equipment for sale or wanted and consultant or laboratory services.**

**Single insertion rate—$15 per column inch.**

**Write to advertising manager for quotation or multiple insertions.**

**Other Society News—** *(Continued from page 88)*

### Course in Modern Industrial Spectrography at Boston College

Boston College July 17-28, 1961

Boston College will again conduct the annual special two-weeks intensive course in spectrography. The course is designed for chemists and physicists from industry who desire to learn the techniques of emission spectroscopy for use in analytical work. For further information, contact Rev. J. J. Devlin, S.J., Dep't. of Physics, Boston College, Chestnut Hill 67, Mass.

### Tenth Annual Conference on Applications of X-Ray Analysis

Denver, Colorado August 7-9, 1961

The conference will be held at the Park Lane Hotel in Denver, Colo. For further information, contact W. M. Mueller, Head, Metallurgy Div., Denver Research Institute, University of Denver, Denver 10, Colorado.

### International Symposium on Far Infrared Spectroscopy

Cincinnati, Ohio August 21-24, 1962

This symposium is being sponsored by the Analytical Branch, Physics Laboratory, Materials Central WADD. Invited papers will be presented by experts on such topics as group frequencies and vibrational assignments, molecular structure, solid state, analytical applications, and instrumentation. For further information, contact E. A. Jenning, University of Dayton Research Institute, Dayton 9, Ohio.

### Mass Spectrometry Conference

Oxford, England September 12-15, 1961

A conference on mass spectrometry will be sponsored by the Mass Spectrometry Panel of the British Institute of Petroleum and Committee E-14 of the American Society for Testing Materials. For further information, contact W. J. Brown, Instrumentation Division, A.E.I. (Manchester) Ltd., Trafford Park, Manchester 17, England.

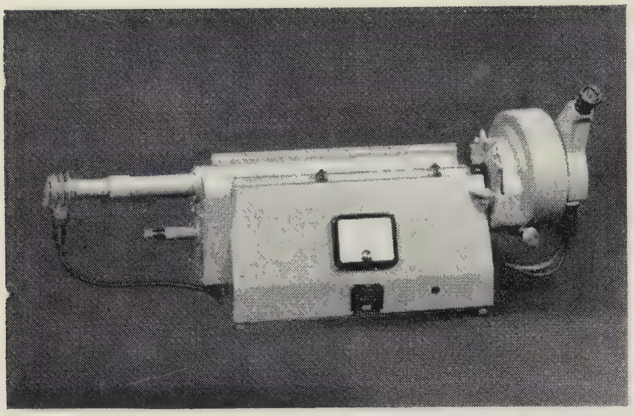
**What's New—** *(Continued from page 13A)* used for this purpose. These include, for example, some absorption lines in the vibration-rotation bands of simple common gases, or the main vibrational peaks of solid polymers. There still remains, however, a degree of non-uniformity among different laboratories, arising in part from small differences in the values adopted for particular standards, and also in part from the fact that the instrumental conditions of measurement are often not taken into account in the calibration operation.

The Commission of Molecular Structure and Spectroscopy of the International Union of Pure and Applied Chemistry has done all spectroscopists a valuable service by collecting together, in a concise little volume, carefully evaluated sets of wavenumbers for use in the range 4000—600 cm$^{-1}$. The members of the Commission are internationally known spectroscopists from ten different countries and they have made an authoritative and critical examination of all the relevant data, much of it very new. The tables are in two parts. The first deals with calibration standards for grating spectrometers of high resolving power. These include atomic emission lines of inert gases or mercury, and rotation lines in vibration bands of simple gases. Details are given for the conversion of wavelengths in air to wavenumbers *in vacuo,* and a brief explanation is given of the effect of pressure, temperature, and other factors. An accuracy of 0.01—0.03 cm$^{-1}$ is the aim but in each case an estimate of the uncertainty is stated. The second part of the report applies to prism spectrometers or small grating instruments, of resolution 0.5—10 cm$^{-1}$. In all, the compilation includes 59 charts and their associated tables of standard line positions. At the end, sets of figures are reproduced in a condensed form, so that it is possible at a glance to decide the best calibrant for any given spectral region.

This book, which is offered at a very modest price, should find a place in all infrared laboratories of any kind as the accepted reference work for many years to come.

*Tables of Wavenumbers,* vi + 163 pp. 96 Figs. An I.U.P.A.C. Publication by Butterworths, Ltd. 4-5 Bell Yard, London W.C. 2, England, 1961, 4-2/10, or Butterworth, Inc., 7235 Wisconsin Av., Washington 14, D.C., U.S.A., $6.00.

CORRECTION—Reprints of *Catalog of I.R. Spectra of Plasticizers* are available at $1.00 per copy from Mr. E. L. Weiss, Leads & Northrop Co., Research and Development Center, Dickerson Rd., No. Wales, Pa. Checks should be made available to the Society for Applied Spectroscopy (cf. *Applied Spectroscopy,* 15, no. 2, 21A (1961)).



M 511—PHOTOELECTRIC POLARIMETER

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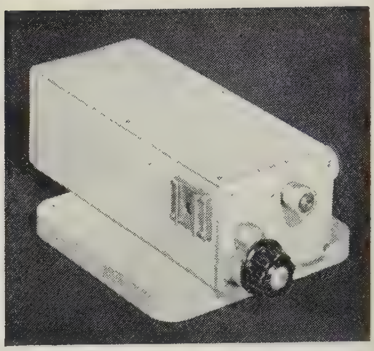

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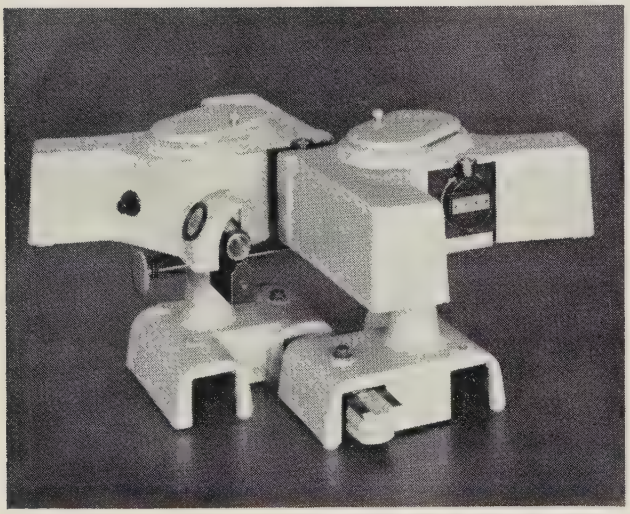
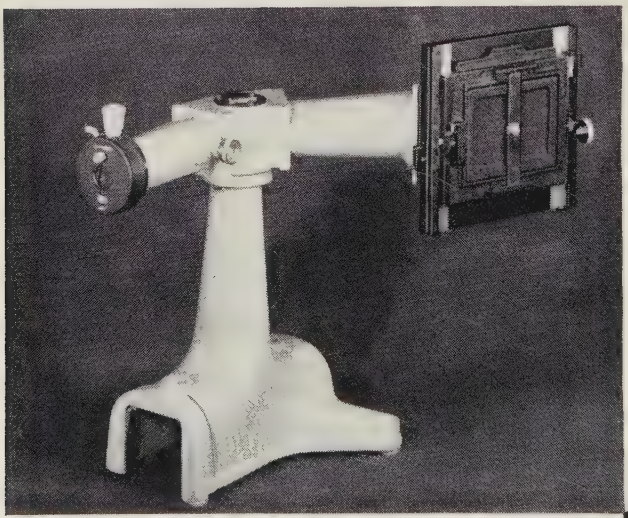


D 284—DOUBLE MONOCHROMATOR



E 584—SMALL PRISM SPECTROGRAPH

### COMPACT GRATING MONOCHROMATOR

D 290—This new, low cost instrument utilizes a 15,000 l.p.i. plane grating covering a spectral range of 2000A to 10,000A with a dispersion of 70A/mm. Can be used vertically or horizontally. Its small size permits combining into other optical systems easily.

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### SMALL PRISM SPECTROGRAPH

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**Spectral Line**—*(Continued from page 9A)* magnetometers, electromagnets, graphic recorders, and other scientific instruments. A graduate of the University of Michigan, Mr. Bell has been associated with Howell Instruments since 1951.

λ

*John F. Moran* has been appointed manager of High Resolution NMR product engineering of Varian Associates. In this capacity, Mr. Moran will be responsible for Varian's nuclear magnetic resonance spectrometers. He is a graduate of the University of California at Berkeley and Stanford University. Mr. Moran joined Varian in 1952 as a junior engineer.

## PUBLICATIONS ACCEPTED

### Papers

S. S. Parker—Infrared Spectra of Vitamins, Schiff Base, and an Amino-Acid Chelate in Water.

E. G. Bendit and D. Ross—Technique for Obtaining the Ultraviolet Absorption Spectrum of Solid Keratin

T. Lee, O. P. Killeen and S. A. MacIntyre — The Spectrographic Determination of Uranium 235. IV.

F. R. McDonald and G. L. Cook —Use of Low Molecular Weight Polyethylene in Ultraviolet Spectroscopy

J. A. Goleb, J. P. Faris, and B. H. Meng—The Spectrochemical Determination of Trace Impurities in Graphite

L. Segal and F. V. Eggerton—The Infrared Spectra of Aliphatic Normal Mono-amines and Alpha-Omega Diamines

D. H. Purcell—The Spectrographic Determination of Molybdenum in Uranium-Molybdenum Alloys

M. F. Grostic and G. E. Bronson—Use of Resolidified Melts in Infrared Spectroscopy. Application to Polymorphism and Solvation Studies

J. N. van Niekerk, F. W. E. Strelow, and F. T. Wybenga—X-ray Spectrographic Determination of Thorium in Low Concentrations

### Notes

A. Strasheim, K. Buijs, and J. van Wamele—A Possible Method of Pulverising Mica and Other Flaking Materials for Spectrographic Analysis

L. Segel and F. V. Eggerton—The Infrared Spectra of Diethylenetriamine and 2-(2-Aminoethylamino)-ethanol

A. A. Ebert, Jr.—Use of a Getter-Ion-Type Pump with a Mass Spectrometer

L. E. Owen—Stable Plasma Jet for Excitation of Solutions

R. J. McGowan — Spectrochemical Analysis of Oils Using "Vacuum Cup" Electrodes

A. J. Kammer, W. H. Washburn, and P. Kurath—A Limitation Regarding the Use of Ethanol Stabilized Chloroform as a Solvent for Infrared Spectroscopy

L. Segal and F. V. Eggerton—Infrared Spectra of Ethylenediamine and the Dimethylethylenediamines

J. L. Monkman—The Longest Wavelength Band in the Ultraviolet Assorption Spectra of the Monomethylbenzanthracenes

### Spectroscopic Tricks

E. M. Banas and R. R. Hopkins—A Sealed Infrared-Absorption Cell of Variable Cell Length

J. J. Kolb—Modification of the Coleman Model 14 Universal Spectrophotometer to Simplify Wavelength Calibration Adjustment

M. L. Gonshor and S. E. Hausknecht—Photo Processing Tank for Spectrographic Plate Development

B. M. Mitzner—"O" Ring Gaskets for Infrared Cells

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**High resolution mass spectrometry. Interpretations of spectra of petroleum fractions.** E. G. Carlson, G. T. Paulissen, R. H. Hunt, and M. J. O'Neal, Jr. Anal. Chem. 32, 1489-94 (Oct. 1960)

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**Spectroscopic investigations on nitroso compounds. III. Dissociation energy of the nitroso dimers.** (In German) V. V. Keusller and W. Luttke. Z. Elektrochem. 63 (no. 5) 614-23 (1959)

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**Grating spectrometer for the Schumann ultraviolet range.** F. J. P. Clarke, and W. R. S. Garton. J. Sci. Instr. 36, 403-8 (Sept. 1959)

**$\beta$-ray spectrometer of toroid-sector type.** A. Szaloy and D. Berenyl. Acta Phys. Acad. Sci. Hung. 10 (no. 1) 57-77 (1959)

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## INTRODUCING THE VARIAN A-60 SPECTROMETER...

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The achievement: reproducible 60 megacycle high-resolution proton spectra that anyone can run. And this is from an instrument smaller, more stable and much lower in cost than any NMR Spectrometer that has existed before. Reproducibility of spectra enables instrument calibration. This means that interpretation, cataloguing, discussion and exchange of NMR information will be greatly facilitated. The spectrometer's new speed and freedom from complexity mean that NMR – a unique physical property and key to abundant molecular information – becomes available to organic chemists everywhere.

**FEATURES**

• Precisely reproducible NMR spectra on precalibrated charts • 1-part-in-$10^8$ resolution at 60 megacycles • Fewer, simpler and more direct controls, enabling operation by nonprofessional personnel • Positive reference to a drift-free standard; controls for sweep ranges, RF amplitude and zero offset all in calibrated steps • Proton spectra only – to provide great reductions in size, complexity and price while giving the NMR capability most universally needed in organic chemistry • Integrator as a built-in standard part of the instrument to provide a quantitative capability • Non-critical environmental requirements and small floorspace needs.

**Price of complete system $23,750**

For complete information, write the Instrument Division

**VARIAN associates**

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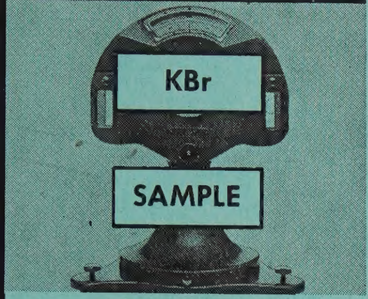
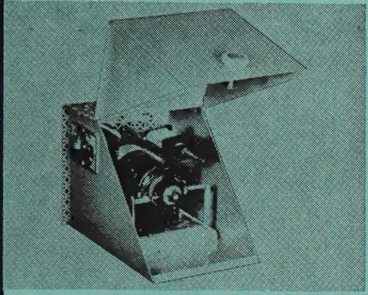
## INFRARED

## SPEXessories

FOR KBr TECHNIQUE



ULTRAMATIC BALANCE



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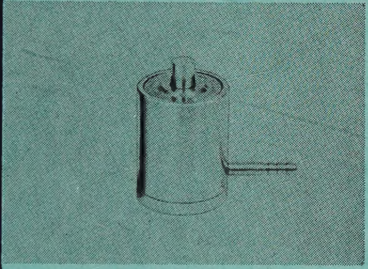
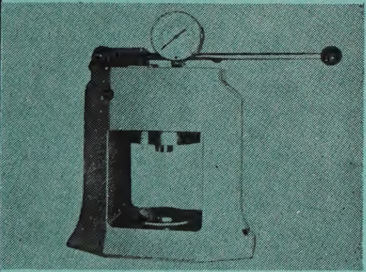


MK. 3 EVACUABLE DIE



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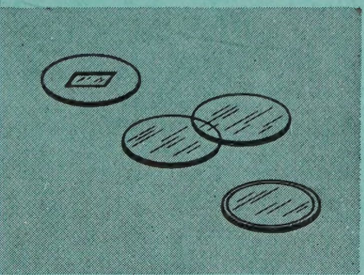

CLEAR, HOMOGENEOUS PELLETS

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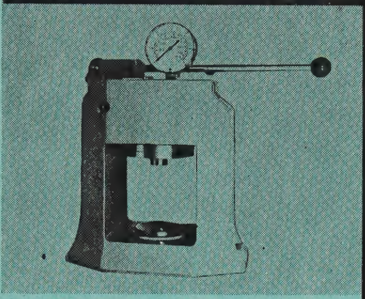
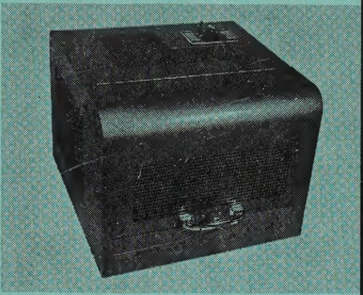
## X-RAY

## SPEXessories

FOR G.E. X-RAY SPECTROMETERS



BRIQUETTING PRESS AND DIES



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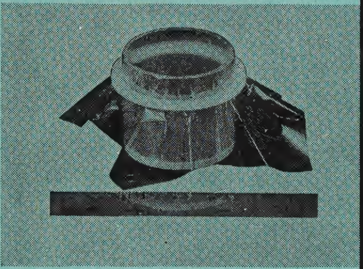
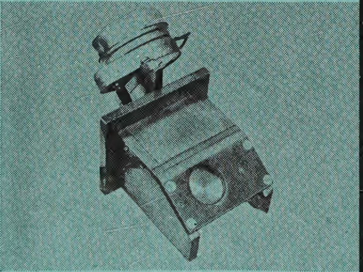
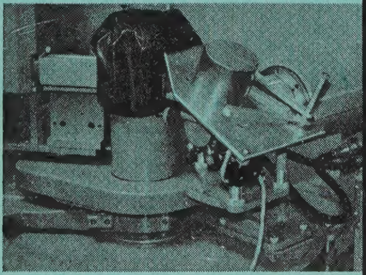


EXPENDABLE LIQUID CELLS



TURNTABLE SAMPLE HOLDER



INVERTED BULK SAMPLE STAND

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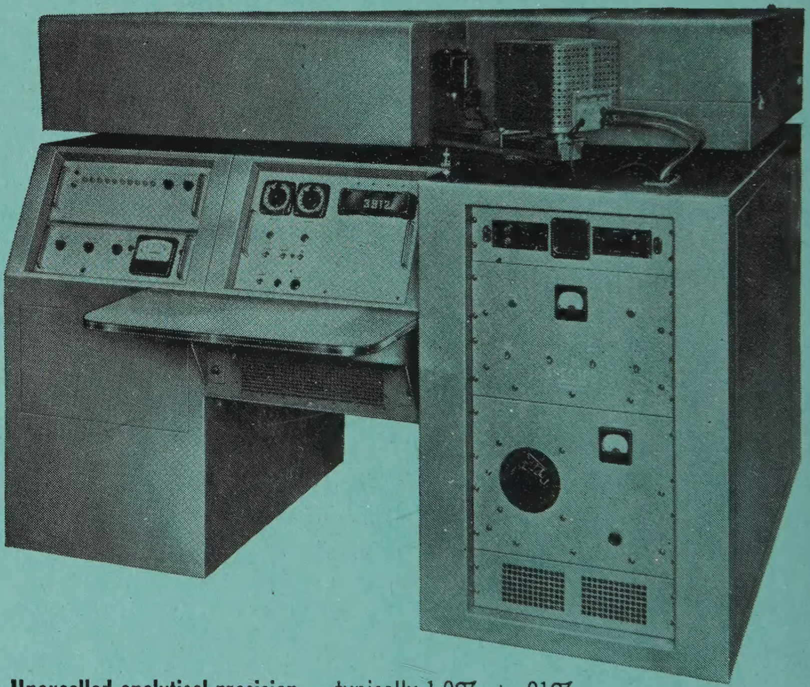

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